Page 1.

ЖУРНАЛ
АНАЛИТИЧЕСКОЙ
ХИМИИ

JOURNAL OF
ANALYTICAL CHEMISTRY
OF THE USSR

(ZHURNAL ANALITICHESKOI KHIMY)

IN ENGLISH TRANSLATION

VOL. XI, 1956 [redacted]

CONSULTANTS BUREAU, INC.

227 WEST 17TH STREET, NEW YORK 11, N. Y.

an agency for the interpretation of international knowledge

THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

(ZHURNAL ANALITICHESKOI KHIMII)

Index to Volume XI, 1956

(A Publication of the Academy of Sciences of the U.S.S.R.)

IN ENGLISH TRANSLATION

Copyright, 1958

CONSULTANTS BUREAU, INC.
227 West 17th Street
New York 11, N. Y.

Printed in the United States

Annual subscription	$ 80.00
Index	5.00

Note: The sale of photostatic copies of any portion of this copyright translation is expressly prohibited by the copyright owners. A complete copy of any paper in this issue can be purchased from the publisher for $ 7.50.

THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE U.S.S.R. IN ENGLISH TRANSLATION

January-February, 1956

TABLE OF CONTENTS

		Page	Russ. Page
1.	The Composition of the Luminescence Center of Sodium Fluoride Beads Activated by Uranium. T. S. Dobrolyubskaya	1	3
2.	The Evaporation Method and Its Use for the Determination of Boron and Other Impurities in Uranium. S. L. Mandelshtam, N. N. Semenov, and Z. M. Turovtseva	7	9
3.	Spectrographic Analysis by the Evaporation Method. I. Principles of the Method of Evaporating Impurities in a Vacuum, and Some of Its Applications. A. N. Zaidel, N. I. Kaliteevsky, L. V. Lipis, M. P. Chaika and Yu. I. Belyaev	17	21
4.	Maintenance of Temperature Conditions During Photo-Colorimetric Determination of Sodium by Means of $NaNi(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$. A. I. Krupkin and G. A. Lorina	25	30
5.	The Specific Character of the Electronic Absorption Spectra of Molecules (The Chromophore Theory). F. Sh. Shifrin	29	33
6.	Sorption of Certain Surface Active Dyes by Sulfides During Aging. N. A. Rudnev, and L. I. Guseva	39	44
7.	The Method of "In Situ Nascendi" Reagents for Determination of the Alkaline Earth Metals. A.P. Terentyev, E. G. Rukhadze and K. I. Litvin	51	55
8.	Oscillographic Polarography on Solid Electrodes. I. I. Tsapiv	59	63
9.	Polarographic Determination of Platinum on Solid Electrodes. II. M. B. Bardin and Yu. S. Lyalikov	63	67
10.	Polarographic Investigation of the Chloride, Bromide, and Thiocyanate Complexes of Cadmium in Absolute Ethyl Alcohol. Ya. I. Turyan	67	71
11.	Microsynthesis and Identification of Some Mercurized Arylamines. I. M. Korenman, and A. A. Belyakov	73	77
12.	Colored Adsorption Reactions of Magnesium Hydroxide. V. I. Kuznetsov	79	81
13.	Analytical Application of the Formation of Hexanitrohydrazobenzene. A. I. Cherkasov and L. M. Kulberg	87	89
14.	A Color Test for the Presence of Linolenic Acid Glycerides in Oils, and a Color Reaction for Certain Organic Compounds with Picric Acid. T. A. Pkheidze and V. P. Goguadze	89	91
15.	The Chromatographic Method in Qualitative Analysis. III. Analysis of As^{3+}, Sb^{3+}, and Sn^{2+}. K. M. Olshanova and K. V. Chmutov	93	94
16.	Accuracy of the Ion-Exchange Method of Standardizing Alkali. Yu. G. Titova	97	99
17.	The Benzoate Method of Aluminum Determination. A. I. Ponomarev and A. Ya. Sheslolskaya	101	102
18.	Quantitative Determination of Boric Acid, Iron, Aluminum Salts When All Are Present Simultaneously. M. B. Shchigol and N. B. Burchinskaya	105	106

TABLE OF CONTENTS (continued)

	Page	Russ. Page
19. Detection of Beryllium When No Precious Metal Vessels Are Available. E. P. Ozhigov and T. I. Vedernikova	111	111

Brief Communications

	Page	Russ. Page
20. A New Method of Detecting Carbon. B. M. Gladshtein	115	114

Chronicle

	Page	Russ. Page
21. Academician Sergei Ivanovich Vavilov and His Role in the Development of Luminescent Analysis. M. Konstantinova-Shlezinger	117	115
22. International Congress on Analytical Chemistry	123	120
23. Analytical Chemistry Committee, V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry	124	120

Announcements

	Page	Russ. Page
24. A New Fluorescent pH Indicator – Dimethylnaphtheirodine	125	Cover
25. A New Chemiluminescent pH Indicator – Luminol	125	Cover
26. Academy of Sciences USSR Press	126	Cover

THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR IN ENGLISH TRANSLATION

March-April, 1956

TABLE OF CONTENTS

	Page	Russ. page
1. Spectrum Analysis by Means of Lines Located in Different Regions of the Spectrum – Method and Theoretical Basis. I. A. Kovalev	127	123
2. Effect of Bulk Composition on the Entry of Individual Test Elements into the Arc Flame. T. F. Borovik-Romanova	133	129
3. Spectrographic Determination of Silicon and Lead in Powder Used for the Production of Synthetic Corundum. O. P. Malkova and N. K. Rudnevsky	139	135
4. High Frequency Titration. III. Analytical Control in the Production of Plastics. B. P. Ershov, V. L. Pokrovskaya, V. A. Zarinsky, and D. I. Koshkin	143	139
5. Polarographic Study of the Electrode Reduction of Niobium and Titanium in Sulfuric Acid Solutions. E. I. Krylov and V. S. Kolevatova	147	144
6. High Frequency Titration. A Q-Metric Analytical Method. Yu. Yu. Samitov	153	149
7. A Chromathermographic Method of Separating Hydrogen, Carbon Monoxide, Methane, and Mixtures of Inert Gases. N. M. Turkeltaub, O. V. Zolotareva, A. G. Latukhova, A. I. Karytova, and E. R. Kalnina	161	159
8. Precipitation Chromatography in Quantitative Analysis. V. D. Kopylova, K. M. Olshanova, and K. V. Chmutov	169	167
9. Detection of Traces of Nickel by Means of Precipitation Chromatography. V. V. Olshanova	173	170
10. A Method for the Analysis of Vanadium Carbides. M. A. Gurevich, B. F. Ormont, and M. Z. Nokhimovskaya	179	177
11. Derivatives of Rhodanine and 2-Thiohydantoin as Reagents for Inorganic Analysis. M. N. Turkevich and V. F. Gevlich	183	180
12. A Cryoscopic Method for the Quantitative Determination of Arenes (Aromatic Hydrocarbons) in Petroleum Oils in Cyclohexane Solution. M D Tilicheev, M. S. Borovaya, and V. S. Buk	191	188
13. A Semi Micro-Quantitative Method for the Individual Determination of the Higher Normal Fatty Acids by Distillation of Their Methyl Esters. L. K. Obukhov	195	193
14. The Analytical Application of Aurintricarboxylic Acid. L. A. Molot and L. M. Kulberg	199	198
15. Quantitative Determination of Ethylene Glycol and Its Monomethyl Ether. I. M. Yurist and Yu. F. Firsova	207	205
16. New Acid-Base Indicators for Low pH Values. V. I. Kuznetsov and G. N. Kosheleva	211	208
17. Color Reactions for Ferricyanides with Dimethylaminoantipyrine and Tetramethyldiaminodiphenylmethane. A. P. Kreshkov, S. S. Vilborg, K. I. Filippova, and V. A. Drozdov	215	212
18. An Analytical Method for Direct and Acid Azo Dyes. B. M. Krasovitsky, B. I. Ostrovskaya, and D. G. Pereyaslova	219	216

TABLE OF CONTENTS (continued)

Page — Russ. page

19. Murexide, its Indicator Properties and a Method for its Preparation. M. M. Sochevanova . . 221 219

20. Rapid Methods of Micro Elemental Analysis. Part IX. Simultaneous Determination of Carbon, Hydrogen, and Silicon in Organo Silicon Compounds. V. A. Klimova, M. O. Korshun, and E. G. Bereznitskaya 225 223

21. New Methods for the Quantitative Determination of Halogens and the Simultaneous Determination of Sulfur and Halogens in Organic Materials. Part III. P. N. Fedoseev and N. P. Ivashova 235 233

22. Determination of the Ammonium Ion by Conductometric Titration. G. B. Pasovskaya . . . 239 237

23. Potentiometric Investigations on Barbiturates. I. The Analytical Characteristics of the Silver Salts of Diethyl-Barbituric Acid (Veronal). Ya. M. Perelman 243 241

24. Photometric and Colorimetric Determination of Thallium as the Hydroxide of Trivalent Thallium. V. K. Zolotukhin and A. S. Molotkova 251 248

Brief Communications

25. A Color Reaction for Cyanides. V. P. Fedotov 253 250

26. Detection of the Cadmium Ion by a Fractional Method. N. S. Shub. 255 251

Review

27. Electrometric pH Determinations. Theory and Practice. Roger G. Bates 257 252

Chronicle

28. Conference on Spectrophotometric and Colorimetric Methods of Analysis 261 254

THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR IN ENGLISH TRANSLATION

May-June, 1956

TABLE OF CONTENTS

Page / Russ. Page

1. A New Gravimetric Method for the Determination of the Nitrite Ion Using Nitriton-B (o-Aminoanilide of Benzene Sulfonic Acid). N.P. Komar and I.U. Martynchenko. 265 259
2. A Microflotation Method of Analyzing Heavy Water. I.P. Gragerov 271 264
3. Separation of Niobium, Tantalum and Titanium by Extraction. F.V. Zaikovsky. . . . 277 269
4. Separation of Magnesium, Aluminum, Chromium, Manganese, Iron, Nickel and Copper by an Ion-Exchange Method. D.I. Ryabchikov and V.F. Osipova 285 278
5. Colorimetric Determination of Traces of Copper in Metallic Nickel and Its Compounds in the Ultra-Violet. K.P. Stolyarov and F.B. Agrest 293 286
6. Rapid Methods of Micro-Elemental Analysis. Part 12. Simultaneous Determination of Carbon, Hydrogen, Silicon and Halides. V.A. Klimova and E.G. Bereznitskaya. . . 299 292
7. Isolation and Separation of a Mixture of Formaldehyde and Acetaldehyde by Means of Dimedone. A.F. Lukovnikov. 305 299
8. Application of β-Hydroxynaphthoic Aldehyde in Analytical Chemistry. Part 2. A New Semi-Micro Gravimetric Method for the Determination of Copper. S.I. Gusev and V.I. Kumov 309 303
9. Chromotropic Azo Dyes as Reagents for Trivalent Thallium. I.M. Korenman, V.G. Potemkina and L.S. Fedorova 313 307
10. Polarographic Determination of Acrylonitrile in Aqueous-Alcohol Solutions. M.N. Platonova 317 310
11. Polarographic Determination on Solid Electrodes of Heavy Metals in the Air of Industrial Establishments. I.B. Kogan 321 313
12. Kinetic Methods of Quantitative Analysis. Part III. Determination of Small Amounts of Molybdenum. K.B. Yatsimirsky and L.P. Afanaseva 327 319
13. Cementation of Certain Metals by Zinc Amalgam. E.F. Speranskaya 331 323
14. A Mercurimetric Method of Determining Iodides. R. Kh. Zamanov. 339 329
15. A Method of Concentrating Traces of Copper by Means of Organic Reagents. V.T. Chuiko and A.U. Mamenko. 343 332
16. The Precipitability of Strontium Oxalate in the Presence of Other Ions. M.P. Babkin 347 337
17. Systematic and Random Errors in Chemical Analysis. V.V. Nalimov. 351 341
18. A Manostat and Receiver for Vacuum Distillation in Columns. M.I. Rosengart, A.L. Liberman and D.M. Dubinin 361 351

Brief Communications

19. The Use of Chromatography in Qualitative Analysis. Stoiko Yankov. 365 355
20. The Dichromate Method of Determining Piperazine. A.A. Chemerisskaya 367 356

TABLE OF CONTENTS (continued)

		Page	Russ. Page
21.	A Fractional Reaction for Cobalt. M.A. Popov	369	357
22.	A New Indicator – Oxine Blue. I.E. Lev	371	359
23.	Detection of Lead in Ores by the Trituration Method. E.P. Ozhigov, M.A. Rafienko and L.K. Ivanenko	373	361
24.	Detection of Fluorine in Minerals and Ores by a Trituration Method. E.P. Ozhigov	375	363
	Chronicle		
25.	Anatoly Kiprilovich Babko (On His Fiftieth Birthday)	377	365
26.	Conference Held in Gorky State University on the Application of Labeled Atoms in Chemistry	381	367
27.	Announcement	383	368

THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR IN ENGLISH TRANSLATION

July-August, 1956

TABLE OF CONTENTS

	Page	Russ page
1. Methods of Isolating Carrier-Free Radioactive Isotopes. Part I. Preparation of Radiochemically Pure ThB and ThC. N. P. Rudenko	385	371
2. Rapid Methods of Micro Elemental Analysis. Part X. Simultaneous Determination of Carbon, Hydrogen and Halogens in Halogen Containing Organic Compounds. M. O. Korshun and N. S. Sheveleva	391	376
3. An Express Drop-Desorption Method for the Separation and Identification of Short-Lived Radio Elements. K. V. Troitsky	399	383
4. Separation of Beryllium from Aluminum and Other Elements by an Extraction Method. I. P. Alimarin and I. M. Gibalo	405	389
5. New Reagents for the Colorimetric Determination of Beryllium – Berillon I and II. A. M. Lukin and G. B. Zavarikhina	409	393
6. Colorimetric Determination of Beryllium by Means of a New Reagent – Berillon II. G. G. Karanovich	417	400
7. New Complexones. Part II. Parafuchsinhexaacetic Acid. R. P. Lastovsky, Yu. I. Vainshtein, N. M. Dyatlova and V. Ya. Temkina	423	405
8. Effect of the Bulk Composition of a Mineral on Results of the Quantitative Determination of Molybdenum in Granitoids. E. E. Vainshtein and L. I. Pavlenko	429	410
9. The Effect of Iron on the Colorimetric Determination of Cerium. R. K. Korabelnik	439	419
10. Accurate Volumetric Determination of Gamma Amounts of Mercury. V. I. Kuznetsov and E. V. Mitrofanova	443	423
11. Coprecipitation of Cadmium with Antipyrine Tetrabromomercuriate. I. M. Korenman and A. A. Tumanov	451	430
12. An Absorption-Precipitation Chromatographic Technique for the Separation of Nickel and Cobalt by Means of Dimethylglyoxime. A. M. Gurevich	459	437
13. The Use of Thiourea Solutions in Volumetric Analysis (Thiocarbamidometry). K. B. Yatsimirsky and A. A. Astasheva	465	442
14. Effect of Temperature on the Rate of Electro-Analysis. V. A. Karnitsky	471	447
15. Analysis of Hypochlorites and Chlorites in Solution. I. E. Flis and M. K. Bynyaeva	477	453
16. Amperometric Titration of Aldehyde with 2,4-Dinitrophenylhydrazone. E. V. Zobov and Yu. S. Lyalikov	483	459
17. Determination of Small Amounts of Acids and Water in Polyorganosiloxane Compounds. S. V. Syavtsillo, B. E. Berezovskaya, N. I. Grinkevich, and O. V. Kloptsova	487	463
18. Potentiometric Investigation of Barbiturates. Part 2. Effect of pH on Complex Formation of Barbiturates with the Silver Ion. Ya. M. Perelman	491	466

TABLE OF CONTENTS (Continued)

	Page	Russ. page
19. A New Method for the Specific Determination of Chlorine. L. M. Kulberg and L. D. Borzova	495	470
20. Microcrystalloscopic Identification of Barbiturates. L. I. Rapaport	503	479
21. A Nomogram for Calculating the Weight of Sample to Take for Determining Molecular Weight Cryoscopically. N. B. Kondukov	507	480
22. Determination of the Degree of Branching of $C_{12}-C_{16}$ Paraffin Hydrocarbons by Infra-Red Spectroscopy. Yu. P. Egorov and Al. A. Petrov	511	483
23. Colorimetric Determination of Sulfide Ions by the Molybdenum-Thiocyanate Reaction. V. A. Nazarenko and M. B. Shustova	517	489
24. Quantitative Determination of Dichlorobenzene Isomers. A. A. Spryskov and Yu. G. Erykalov	521	492
25. The Composition of Uranyl Selenite. A Volumetric Method of Determining Uranium. M. K. Djoshi	525	495

Brief Communications

	Page	Russ. page
26. Methods of Breaking Down Barium Sulfate in Order to Detect the Barium Ion in It Qualitatively. G. I. Barannikov	527	498
27. Photo-Nephelometric Determination of Mercuric Chloride by Means of Urotropine and Potassium Iodide. S. I. Kasyanenko	529	500
28. The Oxalate Method for Detecting Cadmium in the Presence of Copper. M. P. Babkin	533	503
29. Detection of Cadmium in the Presence of Copper. A. D. Despiller, M. A. Gurinovich and Yu. N. Anisimova	537	505
30. Detection of Beryllium Ions. V. K. Zolotukhin	541	508

Discussion

	Page	Russ. page
31. Diffusion of Electrolytes and the Polarographic Method. Reply to Ya. P. Gokhshtein. K. Micka and A. Vlcek	543	510
32. Diffusion of Electrolytes and the Polarographic Method. A Reply to the Preceding Article by K. Micka and A. Vlcek. Ya. P. Gokhshtein	547	513

Chronicle

	Page	Russ. page
33. Aleksei Mikhailovich Vasilev	551	517
34. From the Chemical Nomenclature Commission of the Division of Chemical Sciences of the Academy of Sciences of the USSR	555	519

THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE U.S.S.R. IN ENGLISH TRANSLATION

September-October, 1957

TABLE OF CONTENTS

		Page	Russ. page
1.	Dialkyl- and Diaryldithiophosphoric Acids as Analytical Reagents. Part 1. Potentiometric Determination of Copper by Means of Nickel Diethyldithiophosphate. A. I. Busev and M. I. Ivanyutin	559	523
2.	The Solubility Products of a Number of Arsenates. V. G. Chukhlantsev	565	529
3.	Equilibria in Solutions of Pyrophosphate Complexes. K. B. Yatsimirsky and V. P. Vasilyev	573	536
4.	The Polarographic Catalytic Current of Molybdenum and its Use for Determining Microgram Amounts of Molybdenum. S. I. Sinyakova and M. I. Glinkina	581	544
5.	Colorimetric Determination of Niobium and Tantalum in Ores. F. V. Zaikovsky	591	553
6.	Application of Trihydroxyfluorone Derivatives in Colorimetric Analysis. Determination of Antimony. V. A. Nazarenko and N. V. Lebedeva	599	560
7.	Chromatographic Separation of Radioelements of the Yttrium Group of Elements Obtained During Fission of Ytterbium and Hafnium by High-Energy Protons. A. A. Pozdyakov	605	566
8.	Vanadometric Determination of 5,7-Dibromohydroxyquinoline and Dibromohydroxyquinolates. V. A. Nazarenko and S. Ya. Vinkovetskaya	611	572
9.	Cation-Exchange Properties of Phenol-Formaldehyde Resins in Relation to the Type of Acid Group. E. B. Trostyanskaya, I. P. Losev, and A. S. Tevlina	617	578
10.	Colorimetric Methods of Determining Small Amounts of Thallium. N.T. Voskresenskaya	623	585
11.	Some Questions Relating to the Technique of Radiochemical Experiments. A. A. Goryunov	629	590
12.	Polarographic Determination of Selenium. V. F. Toropova	637	599
13.	Spectra and Spectrophotometric Analysis of Chlorinated Organic Compounds. Part 1. Determination of Chlorex in Admixture with Dichloroethane. Ts. N. Roginskaya and A. I. Finkelshtein	641	602
14.	Chromatographic Separation of Ni^{2+} and Co^{2+} Ions. V. V. Oshchapovsky	645	606
15.	Determination of Small Amounts of Alkoxy Groups in Silico-Organic Compounds. S. V. Syavtsillo and E. A. Bondarevskaya	653	613
16.	Direct Potentiometric Titration of the Sulfate Ion Using the $Mo \mid MoO_3 \| BaSO_4$ Indicator Electrode. Part 1. A. D. Miller	655	615
17.	High-Frequency Argentometric Titration. Yu. Yu. Samitov and V. M. Gorokhovsky	661	621
18.	Spectrographic Determination of Sodium and Potassium in Silicate Rocks. E. E. Vainshtein and V. V. Korolev	667	627

TABLE OF CONTENTS (Continued)

Page Russ. page

Brief Communications

19. An Improved Method of Introducing Test Samples Into the Arc Flame When Working With an Activated AC Arc. T. F. Borovik-Romanova 675 634

20. Excitation of Crystal Formation by Friction During Analytical Reactions. F.M. Kutsakov . 677 636

21. A Quantitative Method of Determining Acrylonitrile by Means of Sodium Sulfite. A. P. Terentyev and S. I. Obtemperanskaya. 681 638

22. Identification of Solid Organic Binary Systems by Means of the Melting Points of the Eutectics. M. Kh. Gluzman and V. P. Rubtsova 683 640

23. Colorimetric Determination of Pyridine in Air. M. I. Tarenko 687 644

Chronicle

24. Abram Semenovich Komarovsky 691 646

25. Conference on the Application of Physicochemical Methods of Analysis and Organic Reagents for Control in the Metallurgical and Metal Working Industries 693 647

26. New Reagent . . . . 695 Back cover

27. Announcement . . . . 695 Back cover

THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE U.S.S.R. IN ENGLISH TRANSLATION

November-December, 1956

TABLE OF CONTENTS

	Page	Russ. Page
1. Studies in the Application of the Counter-Current Distribution Method. Part 1. A Simple Rational Design for the Elementary Cell of a Counter-Current Distribution Apparatus. A. S. Khokhlov and V. M. Baikina	697	651
2. The Use of Phytic Acid in the Analytical Chemistry of Thorium. A. I. Ryabchikov, V. K. Belyaeva, and A. N. Ermakov	705	658
3. Potassium Tetraborate as a Primary Standard in Acidimetry. Ya. Ya. Sauka and Ya. K. Putnin	715	668
4. Spectrophotometric Study of Aqueous Solutions of Quinquevalent Vanadium. Yu. V. Morachevsky and L. I. Belyaeva	719	672
5. Electro-Chemical Behavior of Electrodes During Potentiometric Titration with Trilon B. B. N. Kabanov and L. Ya. Polyak	725	678
6. Organic Coprecipitants (Collectors). Part 7. Coprecipitation of Bismuth. Determination of Small Amounts of Bismuth in Alloys Based on Cr and Ni. V. I. Kuznetsov and L. I. Papushina	733	686
7. Some Properties of Di-β-Naphthylthiocarbazone and Its Bismuth and Nickel Complexes. A. S. Grzhegorzhevsky	737	689
8. Color Reactions for Detecting Cobalt and Bismuth. R. B. Golubtsova	743	694
9. Photometric Determination of Germanium as Germanovanadomolybdic Acid. Z. F. Shakhova and R. K. Motorkina	749	698
10. Polarographic Determination of Palladium on Solid Electrodes. M. B. Bardin and Yu. S. Lyalikov	755	704
11. Amperometric Titration of Zinc, Cobalt, and Copper with Potassium Tetrathiocyanatomercuriate. V. A. Khadeev and A. I. Mirbadaleva	761	710
12. Spectrochemical Determination of Small Amounts of Vanadium in Samples of Complex Composition. T. M. Moroshkina and V. K. Prokofiev	765	714
13. Polarographic Reduction of the Permanganate Ion on Platinum and Mercury Electrodes. O. A. Songina and Z. B. Rozhdestvenskaya	769	717
14. Determination of Very Small Amounts of Nitrate, Nitrite, and Hydroxylamine. N. S. Drozdov and A. K. Iskandaryan	775	723
15. Simultaneous Determination of Carbon, Hydrogen, and Sulfur in Organic Materials. N. V. Sokolova	781	728
16. Potentiometric Methods of Investigating High Molecular Weight Petroleum Compounds. Part 2. A Potentiometric Method of Determining Saponification Numbers in Solutions of Petroleum Resins. S. R. Sergienko, P. N. Galich, N. A. Izmailov, and L. L. Spivak	785	731
17. Titrimetric Determination of Aliphatic and Aromatic Amines with Sodium Tetraphenylboron. A. F. Ievinsh and E. Yu. Gudrinietse	789	735

TABLE OF CONTENTS (continued)

Page Russ. Page

18. Determination of Monoethanolamine, Diethanolamine, and Triethanolamine in Their Mixtures By Partition Chromatography. D. A. Vyakhirev and Yu. N. Suloev 793 739

19. A Photocolorimetric Micro Method of Determining Lactose and Saccharose When They are Present Together. IV. M. N. Tulchinsky 797 742

Brief Communications

20. Methods for the Isotopic Analysis of Water. 1. A New Apparatus for the Falling Drop Method of Isotopic Analysis of Water. A. I. Shatenshtein and Ya. M. Varshavsky 803 746

21. Iodometric Determination of Iodides. B. I. Leonov 807 749

22. A Bismuthate Method for Determining Chromium in Steels not Containing Vanadium. P. F. Agafonov 811 752

23. A New Color Reaction for Divalent Cobalt. G. D. Nessonova and E. K. Pogosyants 813 754

24. A Highly Sensitive Reaction for Hydrogen Peroxide. I. L. Roikh 815 755

Discussion

25. Some Remarks Apropos the Work of I. I. Tsapiv on Oscillographic Polarography. Yu. A. Zotov 817 756

Book Review

26. Extraction Methods in the Laboratory. Hecker 819 758

Obituary

27. Evgeny Stepanovich Przhevalsky 823 761

USSR Academy of Sciences, Chemical Sciences Section

28. Prizes to be Awarded for Competitions by the USSR Academy of Sciences 825 776

AUTHOR INDEX

1956

Afanaseva, L.P., see Yatsimirsky, K.B.
Agafonov, P.F. A bismuthate method for determining chromium in steels not containing vanadium, 811.
Agrest, F.B., see Stolyarov, K.P.
Alimarin, I.P., and I.M. Gibalo. Separation of beryllium from aluminum and other elements by an extraction method, 405.
Anisimova, Yu.N., see Despiller, A.D.
Astasheva, A.A., see Yatsimirsky, K.B.

Babkin, M.P. The oxalate method for detecting cadmium in the presence of copper, 533.
Babkin, M.P. The precipitability of strontium oxalate in the presence of other ions, 347.
Barannikov, G.I. Methods of breaking down barium sulfate in order to detect the barium ion in it qualitatively, 527.
Bardin, M.B., and Yu.S. Lyalikov. Polarographic determination of palladium on solid electrodes, 755.
Bardin, M.D., and Yu.S. Lyalikov. Polarographic determination of platinum on solid electrodes. II., 63.
Belyaev, Yu.I., see Zaidel, A.N.
Belyaeva, V.K., see Ryabchikov, A.I.
Bereznitskaya, E.G., see Klimova, V.A.
Berezovskaya, B.E., see Syavtsillo, S.A.
Bondarevskaya, E.A., see Syavtsillo, S.V.
Borovaya, M.S., see Tilicheev, M.D.
Borovik-Romanova, T.F. An improved method of introducing test samples into the arc flame when working with an activated A.C. arc, 675.
Borovik-Romanova, T.F. Effect of bulk composition on the entry of individual test elements into the arc flame, 133.
Borzova, L.D., see Kulberg, L.M.
Buk, V.S., see Tilicheev, M.D.
Burchinskaya, N.B., see Shchigol, M.B.
Busev, A.I., and M.I. Ivanyutin. Dialkyl- and diaryldithiophosphoric acids as analytical reagents. Part 1. Potentiometric determination of copper by means of nickel diethyldithiophosphate, 559.
Busev, A.I., and N.G. Polyansky. Book review. Electrometric pH determinations. Theory and practice. R.G. Bates (1954), 257.
Busev, A.I., and N.G. Polyansky. Book review. Extraction methods in the laboratory. Hecker (1955), 819.
Busev, A.I., and N.G. Polyansky. Obituary, Evgeny Stepanovich Przhevalsky, 823.
Bynyaeva, M.K., see Flis, I.E.

Chaika, M.P., see Zaidel, A.N.
Chemerisskaya, A.A. The dichromate method of determining piperazine, 367.
Cherkasov, A.I., and L.M. Kulberg. Analytical application of the formation of hexanitrohydrazobenzene, 87.
Chmutov, K.V., see Kopylova, V.D.
Chmutov, K.V., see Olshanova, K.M.
Chuiko, V.T. and A.U. Mamenko. A method of concentrating traces of copper by means of organic reagents, 343.
Chukhlantsev, V.G. The solubility products of a number of arsenates, 565.

Despiller, A.D., M.A. Gurinovich and Yu. N. Anisimova. Detection of cadmium in the presence of copper, 537.
Djoshi, M.K. The composition of uranyl selenite. A volumetric method of determining uranium, 525.
Dobrolyubskaya, T.S. The composition of the luminescence center of sodium fluoride beads activated by uranium, 1.
Drozdov, N.S., and A.K. Iskandaryan. Determination of very small amounts of nitrate, nitrite and hydroxylamine, 775.
Drozdov, V.A., see Kreshkov, A.P.
Dyatlova, N.M., see Lastovsky, R.P.

Egorov, Yu.P., and Al. A. Petrov. Determination of the degree of branching of C_{12}-C_{16} paraffin hydrocarbons by infra-red spectroscopy, 511.
Ermakov, A.N., see Ryabchikov, A.I.
Ershov, B.P., V.L. Pokrovskaya, V.A. Zarinsky and D.I. Koshkin. High frequency titration. III. Analytical acontrol in the production of plastics, 143.
Erykalov, Yu. G., see Spryskov, A.A.

Fedorova, L.S., see Korenman, I.M.
Fedoseev, P.N., and N.P. Ivashova. New methods for the quantitative determination of halogens and the simultaneous determination of sulfur and halogens in organic materials. Part III., 235.
Fedotov, V.P. A color reaction for cyanides, 253.
Filippova, K.I., see Kreshkov, A.P.

Finkelshtein, A.I., see Roginskaya, Ts. N.

Firsova, Yu.F., see Yurist, I.M.

Flis, I.A., and M.K. Bynyaeva. Analysis of hypochlorites and chlorites in solution, 477.

Galich, P.N., see Sergienko, S.R.

Gevlich, V.F., see Turkevich, N.M.

Gibalo, I.M., see Alimarin, I.P.

Gladshtein, B.M. A new method of detecting carbon, 115.

Glinkina, M.I., see Sinyakova, S.I.

Gluzman, M.Kh., and V.P. Rubtsova. Identification of solid organic binary systems by means of the melting points of the eutectics, 683.

Goguadze, V.P., see Pkheidze, T.A.

Gokhstein, Ya.P. Diffusion of electrolytes and the polarographic method. A reply to the preceding article by K. Micka and A. Vlcek, 547.

Golubtsova, R.B. Color reactions for detecting cobalt and bismuth, 743.

Gorokhovsky, V.M., see Samitov, Yu.Yu.

Goryunov, A.A. Some questions relating to the technique of radiochemical experiments, 629.

Gragerov, I.P. A microflotation method of analyzing heavy water, 271.

Grinkevich, N.I., see Syavitsillo, S.V.

Grzhegorzhevsky, A.S. Some properties of di-β-naphthylthiocarbazone and its bismuth and nickel complexes, 737.

Gurevich, A.M. An absorption-precipitation chromatographic technique for the separation of nickel and cobalt by means of dimethylglyoxime, 459.

Gurevich, M.A., B.F. Ormont and M.Z. Nokhimovskaya. A method for the analysis of vanadium carbides, 179.

Gurinovich, M.A., see Despiller, A.D.

Gusev, S.I., and V.I. Kumov. Application of β-hydroxynaphthoic aldehyde in analytical chemistry. Part 2. A new semi-micro gravimetric method for the determination of copper, 309.

Guseva, L.I., see Rudnev, N.A.

Ievinsh, A.F., and E.Yu. Gudrinietse. Titrimetric determination of aliphatic and aromatic amines with sodium tetraphenylboron, 789.

Iskandaryan, A.K., see Drozdov, N.S.

Ivanenko, L.K., see Ozhigov, E.P.

Ivanyutin, M.I., see Busev, A.I.

Ivashova, N.P., see Fedoseev, P.N.

Izmailov, N.A., see Sergienko, S.R.

Kabanov, B.N., and L.Ya. Polyak. Electrochemical behavior of electrodes during potentiometric titration with Trilon B, 725.

Kaliteevsky, N.I., see Zaidel, A.N.

Kalnina, E.R., see Turkeltaub, N.M.

Karanovich, G.G. Colorimetric determination of beryllium by means of a new reagent Berillon II, 417.

Karnitsky, V.A. Effect of temperature on the rate of electro-analysis, 471.

Karytova, A.I., see Turkeltaub, N.M.

Kasyanenko, S.I. Photo-nephelometric determination of mercuric chloride by means of urotropine and potassium iodide, 529.

Khadeev, V.A., and A.I. Mirbadaleva. Amperometric titration of zinc, cobalt and copper with potassium tetrathiocyanatomercuriate, 761.

Khokhlov, A.S., and V.M. Baikina. Studies in the application of the counter-current distribution method. Part 1. A simple rational design for the elementary cell of a counter-current distribution apparatus, 697.

Klimova, V.A., and E.G. Bereznitskaya. Rapid methods of micro-elemental analysis. Part 12. Simultaneous determination of carbon, hydrogen, silicon and halides, 299.

Klimova, V.A., M.O. Korshun and E.G. Bereznitskaya. Rapid method of micro elemental analysis. Part IX. Simultaneous determination of carbon, hydrogen and silicon in organo-silicon compounds, 225.

Kloptsova, O.V., see Syavitsillo, S.V.

Kogan, I.B. Polarographic determination on solid electrodes of heavy metals in the air of industrial establishments, 321.

Kolevatova, V.S., see Krylov, E.I.

Komar, N.P., and I.Yu. Martynchenko. A new gravimetric method for the determination of the nitrite ion using Nitriton-B (o-amino-anilide of benzenesulfonic acid), 265.

Kondukov, N.B. A nomogram for calculating the weight of sample to take for determining molecular weight cryoscopically, 507.

Konstantinova-Shlezinger, M. Academician Sergei Ivanovich Vavilov and his role in the development of luminescent analysis, 117.

Kopylova, V.D., K.M. Olshanova and K.V. Chmutov. Precipitation chromatography in quantitative analysis, 169.

Korabelnik, R.K. The effect of iron on the colorimetric determination of cerium, 439.

Korenman, I.M. Conference held in Gorky State University on the application of labeled atoms in chemistry, 381.

Korenman, I.M. and A.A. Belyakov. Microsynthesis and identification of some mercurized arylamines, 73.

Korenman, I.M., V.G. Potemkina and L.S. Fedorova. Chromotropic azo dyes as reagents for trivalent thallium, 313.

Korenman, I.M., and A.A. Tumanov. Coprecipitation of cadmium with antipyrine tetrabromomercuriate, 451.

Korolev, V.V., see Vainshtein, E.E.

Korshun, M.O., see Klimova, V.A.

Korshun, M.O., and N.S. Sheveleva. Rapid methods of micro elemental analysis. Part X. Simultaneous determination of carbon, hydrogen and halogens in halogen-containing organic compounds, 391.

Kosheleva, G.N., see Kuznetsov, V.I.

Koshkin, D.I., see Ershov, B.P.

Kovalev, I.A. Spectrum analysis by means of lines located in different regions of the spectrum—method and theoretical basis, 127.

Krasovitsky, B.M., B.I. Ostrovskaya and D.G. Pereyaslova. An analytical method for direct and acid azo dyes, 219.

Kreshkov, A.P., S.S. Vilborg, K.I. Filippova and V.A. Drozdov. Color reactions for ferricyanides with dimethylamino-antipyrine and tetramethyldiaminodiphenylmethane, 215.

Krupkin, A.I., and G.A. Lorina. Maintenance of temperature conditions during photocolorimetric determination of sodium by means of $NaNi(UO_2)_3(CH_3COO)_9 \cdot 6\,H_2O$, 25.

Krylov, E.I., and V.S. Kolevatova. Polarographic study of the electrode reduction of niobium and titanium in sulfuric acid solutions, 147.

Kulberg, L.M., and L.D. Borzova. A new method for the specific determination of chlorine, 495.

Kulberg, L.M., see Cherkasov, A.I.

Kulberg, L.M., see Molot, L.A.

Kumov, V.I., see Gusev, S.I.

Kutsakov, F.M. Excitation of crystal formation by friction during analytical reactions, 677.

Kuznetsov, V.I. Colored adsorption reactions of magnesium hydroxide, 79.

Kuznetsov, V.I., and G.N. Kosheleva. New acid-base indicators for low pH values, 211.

Kuznetsov, V.I., and E.V. Mitrofanova. Accurate determination of gamma amounts of mercury, 443.

Kuznetsov, V.I., and L.I. Papushina. Organic coprecipitants (collectors). Part 7. Coprecipitation of bismuth. Determination of small amounts of bismuth in alloys based on Cr and Ni, 733.

Lastovsky, R.P., Yu. I. Vainshtein, N. M. Dyatlova and V.Ya. Temkina. New complexones Part II. Parafuchsinhexaacetic acid, 423.

Latukhova, A.G., see Turkeltaub, N.M.

Leonov, B.I. Iodometric determination of iodides, 807.

Lev, I.E. A new indicator—oxine blue, 371.

Lipis, L.V., see Zaidel, A.N.

Litvin, K.I., see Terentyev, A.P.

Lorina, G.A., see Krupkin, A.I.

Losev, I.P., see Trostyanskaya, E.B.

Lukin, A.M., and G.B. Zavarikhina. New reagents for the colorimetric determination of beryllium— Berillon I and II, 409.

Lukovnikov, A.F. Isolation and separation of a mixture of formaldehyde and acetaldehyde by means of dimedone, 305.

Lyalikov, Yu.S., see Bardin, M.B.

Lyalikov, Yu.S., see Zobov, E.V.

Malkova, O.P., and N.K. Rudnevsky. Spectrographic determination of silicon and lead in powder used for the production of synthetic corundum, 139.

Mamenko, A.U., see Chuiko, V.T.

Mandelshtam, S.L., N.N. Semenov and Z.M. Turovtseva. The evaporation method and its use for the determination of boron and other impurities in uranium, 7.

Martynchenko, I.Yu., see Komar, N.P.

Micka, K., and A. Vlcek. Diffusion of electrolytes and the polarographic method. Reply to Ya. P. Gokhstein, 543.

Miller, A.D. Direct potentiometric titration of the sulfate ion using the Mo MoO_3 $BaSO_4$ indicator electrode. Part 1, 655.

Mirbadaleva, A.I., see Khadeev, V.A.

Mitrofanova, E.V., see Kuznetsov, V.I.

Molot, L.A., and L.M. Kulberg. The analytical application of aurintricarboxylic acid, 199.

Morachevsky, Yu. V., and L.I. Belyaeva. Spectrophotometric study of aqueous solutions of quinquevalent vandium, 719.

Moroshkina, T.M., and V.K. Prokofiev. Spectrochemical determination of small amounts of vanadium in samples of complex composition, 765.

Motorkina, R.K., see Shakhova, Z. F.

Nalimov, V.V. Systematic and random errors in chemical analysis, 351.

Nazarenko, V.A., and N.V. Lebedeva. Application of trihydroxyfluorone derivatives in colorimetric analysis. Determination of antimony, 599.

Nazarenko, V.A., and M.B. Shustova. Colorimetric determination of sulfide ions by the molybdenum-thiocyanate reaction, 517.

Nazarenko, V.A., and S.Ya. Vinkovetskaya. Vanadometric determination of 5,7-dibromohydroxyquinoline and dibromohydroxyquinolates, 611.

Nessonova, G.D. and E.K. Pogosyants. A new color reaction for divalent cobalt, 813.

Nokhimovskaya, M.Z., see Gurevich, M.A.

Obukhov, L.K. Semi micro-quantitative method for the individual determination of the higher normal fatty acids by distillation of their methyl esters, 195.

Olshanova, K.M., and K.V. Chmutov. The chromatographic method in qualitative analysis. III. Analysis of A_s^{3+} · Sb^{3+} and Sn^{2+}, 93.

Olshanova, K.M., see Kopylova, V.D.

Olshanova, V.V. Detection of traces of nickel by means of precipitation chromatography, 173.

Ormont, B.F., see Gurevich, M.A.

Oshchapovsky, V.V. Chromatographic separation of Ni^{2+} and Co^{2+} ions, 645.

Osipova, V.F., see Ryabchikov, D.I.

Ostrovskaya, B.I., see Krasovitsky, B.M.

Ozhigov, E.P. Detection of fluorine in minerals and ores by a trituration method, 375.

Ozhigov, E.P., M.A. Rafienko and L.K. Ivanenko. Detection of lead in ores by the trituration method, 373.

Ozhigov, E.P., and T.I. Vedemikova. Detection of beryllium when no precious metal vessels are available, 111.

Papushina, L.I., see Kuznetsov, V.I.

Pasovskaya, G.B. Determination of the ammonium ion by conductometric titration, 239.

Pavlenko, L.I., see Vainshtein, E.E.

Perelman, Ya. M. Potentiometric investigations on barbiturates. 1. The analytical characteristics of the silver salts of diethyl-barbituric acid (veronal), 243.

Perelman, Ya. M. Potentiometric investigation of barbiturates. Part 2. Effect of pH on complex formation of barbiturates with the silver ion, 491.

Pereyaslova, D.G., see Krasovitsky, B.M.

Petrov, Al. A., see Egorov, Yu.P.

Phkeidze, T.A., and V.P. Goguadze. A color test for the presence of linolenic acid glycerides in oils, and a color reaction for certain organic compounds with picric acid, 89.

Platonova, M.N. Polarographic determination of acrylonitrile on aqueous – alcohol solutions, 317.

Pogosyants, E.K., see Nessonova, G.D.

Pokrovskaya, V.L., see Ershov, B.P.

Polyak, L.Ya., see Kabanov, B.N.

Polyansky, N.G., see Busev, A.I.

Ponomarev, A.I., and A.Ya. Sheslolskaya. The benzoate method of aluminum determination, 101.

Popov, M.A. A fractional reaction for cobalt, 369.

Potemkina, V.G., see Korenman, I.M.

Pozdyakov, A.A. Chromatographic separation of radioelements of the yttrium group of elements obtained during fussion of ytterbium and hafnium by high energy protons, 605.

Prokofiev, V.K., see Moroshkina, T.M.

Putnin, Ya. K., see Suaka, Ya. Ya.

Rafienko, M.A., see Ozhigov, E.P.

Rapaport, L.I. Microcrystalloscopic identification of barbiturates, 503.

Roginskaya, Ts. N., and A.I. Finkelshtein. Spectra and spectrophotometric analysis of chlorinated organic compounds. Part 1. Determination of chlorex in admixture with dichloroethane, 641.

Roikh, I.L. A highly sensitive reaction for hydrogen peroxide, 815.

Rosengart, M.I., A.L. Liberman and D.M. Dubinin. A manostat and receiver for vacuum distillation in columns, 361.

Rozhdestvenskaya, Z.B., see Songina, O.A.

Rudenko, N.P. Methods of isolating carrier free radioactive isotopes. Part 1. Preparation of radiochemically pure ThB and ThC, 385.

Rudnev, N.A., and L.I. Guseva. Sorption of certain surface active dyes by sulfides during aging, 39.

Rudnevsky, N.K., see Malkova, O.P.

Rukhadze, E.G., see Terentyev, A.P.

Ryabchikov, A.I., V.K. Belyaeva and A.N. Ermakov. The use of phytic acid in the analytical chemistry of thorium, 705.

Ryabchikov, D.I., and V. F. Osipova. Separation of magnesium, aluminum, chromium, manganese, iron, nickel and copper by an ion-exchange method, 285.

Samitov, Yu.Yu. High frequency titration. A Q-metric analytical method, 153.

Samitov, Yu.Yu., and V.M. Gorokhovsky. High-frequency argentometric titration, 661.

Sauka, Ya.Ya., and Ya.K. Putnin. Potassium tetraborate as a primary standard in acidimetry, 715.

Semenov, N.N., see Mandelshtam, S.L.

Sergienko, S.R., P.N. Galich, N.A. Ismailov and L.L. Spivak. Potentiometric methods of investigating high molecular weight petroleum compounds. Part 2. A potentiometric method of determining saponification numbers in solutions of petroleum resins, 785.

Shakhova, Z.F., and R.K. Motorkina. Photometric determination of germanium as germanovanadomolybdic acid, 749.

Shatenshtein, A.I., and Ya.M. Varshavsky. Methods for the isotopic analysis of water. 1. A new apparatus for the falling-drop method of isotopic analysis of water, 803.

Shchigol, M.B., and N.B. Burchinskaya. Quantitative determination of boric acid, iron, aluminum salts when all are present simultaneously, 105.

Sheslolskaya, A.Ya., see Ponomarev, A.I.

Sheveleva, N.S., see Korshun, M.O.

Shifrin, F.Sh. The specific character of the electronic absorption spectra of molecules (the chromophore theory), 29.

Shub, N.S. Detection of the cadmium ion by a fractional method, 255.

Shustova, M.B., see Nazarenko, V.A.

Sinyakova, S.I., and M.I. Glinkina. The polarographic catalytic current of molybdenum and its use for determining micro-gram amounts of molybdenum, 581.

Sochevanova, M.M. Murexide, its indicator properties and a method for its preparation, 221.

Sokolova, N.V. Simultaneous determination of carbon, hydrogen and sulfur in organic materials, 781.

Songina, O.A., and Z.B. Rozhdestvenskaya. Polarographic reduction of the permanganate ion on platinum and mercury electrodes, 769.

Speranskaya, E.F. Cementation of certain metals by zinc amalgam, 331.

Spivak, L.L., see Sergienko, S.R.

Spryskov, A.A., and Yu.G. Erykalov. Quantitative determination of dichlorobenzene isomers, 521.

Stolyarov, K.P., and F.B. Agrest. Colorimetric determination of traces of copper in metallic nickel and its compounds in the ultra-violet, 293.

Syavtsillo, S.V., B.E. Berezovskaya, N.I. Grinkevich and O.V. Kloptsova. Determination of small amounts of acids and water in polyorganosiloxane compounds, 487.

Syavtsillo, S.V., and E.A. Bondarevskaya. Determination of small amounts of alkoxy groups in silico-organic compounds, 653.

Tarenko, M.I. Colorimetric determination of pyridine in air, 687.

Temkina, V.Ya., see Lastovsky, R.P.

Terentyev, A.P., E.G. Rukhadze and K.I. Litvin. The method of "in situ nascendi" reagents for determination of the alkaline earth metals, 51.

Terentyev, A.P., and S.I. Obtemperanskaya. A quantitative method of determining acrylonitrile by means of sodium sulfite, 681.

Tevlina, A.S., see Trostyanskaya, E.B.

Tilicheev, M.D., M.S. Borovaya and V.S. Buk. A cryoscopic method for the quantitative determination of arenes (aromatic hydrocarbons) in petroleum oils in cyclohexane solution, 191.

Titova, Yu.G. Accuracy of the ion-exchange method of standardizing alkali, 97.

Toropova, V.F. Polarographic determination of selenium, 637.

Troitsky, K.V. An express drop-desorption method for the separation and identification of short-lived radioelements, 399.

Trostyanskaya, E.B., I.P. Losev, and A.S. Tevlina. Cation-exchange properties of phenol-formaldehyde resins in relation to the type of acid group, 617.

Tsapiv, I.I. Oscillographic polarography on solid electrodes, 59.

Tuichinsky, M.N. Photocolorimetric micro method of determining lactose and saccharose when they are present together IV, 797.

Tumanov, A.A., see Korenman, I.M.

Turkeltaub, N.M., O.V. Zolotareva, A.G. Latukhova, A.I. Karytova and E.R. Kalnina. A chromatothermographic method of separating hydrogen, carbon monoxide, methane and mixtures of inert gases, 161.

Turkevich, N.M., and V.F. Gevlich. Derivatives of rhodanine and 2-thiohydantoin as reagents for inorganic analysis, 183.

Turovtseva, Z.M., see Mandelshtam, S.L.

Turyan, Ya. L. Polarographic investigation of the chloride, bromide and thiocyanate complexes of cadmium in absolute ethyl alcohol, 67.

Baikina, V.M., see Khokhlov, A.S.

Vainshtein, E.E. and V.V. Korolev. Spectrographic determination of sodium and potassium in silicate rocks, 667.

Vainshtein, Yu. I., see Lastovsky, R.P.

Vainshtein, E.E., and L.I. Pavlenko. Effect of the bulk composition of a mineral on results of the quantitative determination of molybdenum in granitoids, 429.

Varshavsky, Ya.M.,see Shatenshtein, A.I.

Vasilyev, V.P., see Yatsimirsky, K.B.

Vavilov, Academician Sergei Ivanovich, and his role in the development of luminescent analysis. In commemoration of his death five years ago, 117.

Vedernikova, T.I., see Ozhigov, E.P.

Vilborg, S.S., see Kreshkov, A.P.

Vinkovetskaya, S.Ya., see Nazarenko, V.A.

Vlcek, A., see Micka, K.

Voskresenskaya, N.T. Colorimetric methods of determining small amounts of thallium, 623.

Vyakhirev, D.A. and Yu.N. Suloev. Determination of monoethanolamine, diethanolamine, and triethanolamine in their mixtures by partition chromatography, 793.

Yankov, Stoiko. The use of chromatography in qualitative analysis, 365.

Yatsimirsky, K.B., and L.P. Afanaseva. Kinetic methods of quantitative analysis. Part III. Determination of small amounts of molybdenum, 327.

Yatsimirsky, K.B., and A.A. Astasheva. The use of thiourea solutions in volumetric analysis (thiocarbamidometry), 465.

Yatsimirsky, K.B., and V.P. Vasilyev. Equilibria in solutions of pyrophosphate complexes, 573.

Yurist, I.M., and Yu.F. Firsova. Quantitative determination of ethylene glycol and its monomethyl ether, 207.

Zaidel, A.N., N.I. Kaliteevsky, L.V. Lipis, M.P. Chaika and Yu.I. Belyaev. Spectrographic analysis by the evaporation method. I. Principles of the method of evaporation of impurities in a vacuum and some of its applications, 17.

Zaikovsky, F.V. Colorimetric determination of niobium and tantalum in ores, 591.

Zaikovsky, F.V. Separation of niobium, tantalum and titanium by extraction, 277.

Zamanov, R.Kh. A mercurimetric method of determining iodides, 339.

Zarinsky, V.A., see Ershov, B.P.

Zavarikhina, G.B., see Lukin, A.M.

Zobov, E.V., and Yu.S. Lyalikov. Amperometric titration of aldehyde with 2,4-dinitrophenylhydrazone, 483.

Zolotareva, O.V., see Turkeltaub, N.M.

Zolotukhin, V.K. Detection of beryllium ions, 541.

Zolotukhin, V.K., and A.S. Molotkova. Photometric and colorimetric determination of thallium as the hydroxide of trivalent thallium, 251.

Zotov, Yu.A. Some remarks apropos the work of I.I. Tsapiv on oscillographic polarography, 817.

SUBJECT INDEX

1956

Academy of Sciences, USSR, Chemical Sciences Section. Prizes to be awarded for competitions, 825.
Acetaldehyde, mixture with formaldehyde, isolation and separation with Dimedone, 305.
Acetone, acetyl, use in separation of beryllium from aluminum and other elements, 405.
Acid. Aurintricarboxylic, analytical application of, in the form of its ammonium salt (Aluminon), 199.
— Benzenesulfonic, o-aminoanilide of, (Nitriton B), for determination of nitrite ion by gravimetric method, 265.
— Germanovanadomolybdic, and photometric determination of germanium, 749.
— Parafuchsinhexaacetic, see complexones.
Acidimetry, use of potassium tetraborate as a primary standard in, 715.
Acids. Fatty, higher normal, semi microquantitative method for the individual determination of, by distillation of their methyl esters, 195.
— Hydrochloric, sulfuric, determination of small amounts in polyorganosiloxane compounds, 487.
Acrylonitrile, polarographic determination in aqueous alcohol solutions, 317.
Acrylonitrile, quantitative method of determination using sodium sulfite, 681.
Aldehyde, β-hydroxynaphthoic, use in analytical chemistry. A new semi-micro gravimetric method for the determination of copper, 309.
Aldehydes, Amperometric titration of, using 2,4-dinitrophenylhydrazine, 483.
Alkali, Ion-exchange method of standardizing, accuracy of, 97.
Alkoxy groups, Determination of small amounts of, in silico-organic compounds, 653.
Alloys, Cr-Ni, determination of small amounts of bismuth in, by coprecipitation, 733.
Aluminon, See acid, aurintricarboxylic.
Aluminum. As reagent for the detection of cadmium in the presence of copper, 537.
— Determination by the benzoate method, in presence of iron, in ores, minerals and industrial products, 101.
— Separation by an ion-exchange method, 285.
— Oxide, used for the production of synthetic corundum, spectrographic determination of lead and silicon in, 139.
— Salts, quantitative determination in presence of boric acid and iron, 105.
Amalgam, zinc, cementation of metals by, 331.
Amines. Aliphatic, aromatic, titrimetric determination with sodium tetraphenylboron, 789.
— Aryl, mercurized, microsynthesis and identification, 73.
Ammonium ion, determination by conductometric titration, 239.
Ammonium oxalate, for detecting cadmium in the presence of copper, 533.
Amperometric analysis, Amperometric titration of zinc, cobalt and copper with potassium tetrathiocyanatomercuriate, 761.
Anilide, o-amino, of benzenesulfonic acid, see acid, benzenesulfonic.
Announcement of publication of papers on spectrophotometric and colorimetric methods of analysis by USSR Academy of Sciences, 383.
Antibiotics. Application of the counter-current distribution method, design of cell, 697.
Antimony. Colorimetric determination with phenylfluorone, 599.
— Qualitative chromatographic method for, in presence of arsenic and tin, 93.
Antipyrine, Dimethylamino, for detection of ferricyanides, 215.
— Tetrabromomercuriate, use for coprecipitation of cadmium, 451.
Arc flame, effect of bulk composition on the entry of individual test elements into, 133.
Arenes, see hydrocarbons, aromatic.
Arsenates, solubility products of, 565.
Arsenic, Qualitative chromatographic method for, in presence of antimony and tin, 93.

Babko, Anatoly Kiprilovich, fiftieth birthday of, 377.
Barbiturates. Effect of pH on complex formation of, with the silver ion, 491.
— Microcrystalloscopic identification of, 503.
Barbituric acid, diethyl, silver salts, analytical characteristics of, (potentiometric investigations), 243.
Barium sulfate, Methods of breaking down in order to detect the barium ion in it qualitatively, 527.
Benzaldehyde, determination by amperometric titration using 2,4-dinitrophenylhydrazine, 483.
Benzene. Dichloro, isomers. Quantitative determination of, 521.
— Hexanitrohydrazo, analytical applications of the formation of, 87.

Berillon I, II, new reagents for the colorimetric determination of beryllium, preparation, 409.
Berillon II, a new reagent for tne colorimetric determination of beryllium, preparation, 417.
Beryllium. Colorimetric determination by means of a new reagent — Berillon II, 417.
— Detection when no precious metal vessels are available, 111.
— New reagents for the colorimetric determination of — Berillon I and II, 409.
— separation from aluminum and other elements by an extraction method using acetylacetone and Trilon B, 405.
Beryllium ions, detection of, based on interaction of beryllium hydroxide with alkali metal fluorides, 541.
Biochemistry, Determination of very small amounts of nitrate, nitrite and hydroxylamine, 775.
Bismuth. Color reaction with β-naphthoxyquinoline for macro- and microchemical detection, 743.
— Coprecipitation of. Determination of small amounts of bismuth in alloys based on Cr and Ni, 733.
— complex of di-β-naphthylthiocarbazone, see thiocarbazone, di-β-naphthyl.
Book review. Electrometric pH determinations. Theory and practice. R. G. Bates (1954), 257.
— Extraction methods, Hecker (1955), 819.
Books, recent and older publications, Academy of Sciences USSR Press, 126.
Boric acid, quantitative determination in presence of iron, aluminum salts, 105.
Boron, and other impurities in uranium, determination by the evaporation method, 7.
Boron organic compounds. Titrimetric determination of aliphatic and aromatic amines with sodium tetraphenylboron, 789.

Cadmium, Coprecipitation with antipyrine tetrabromomercuriate, 451.
— Detection in presence of copper by the oxalate method, 533.
— Detection in presence of copper, using metallic aluminum, 537.
— Volumetric analysis with thiourea solutions, 465.
— Chloride, bromide and thiocyanate complexes, polarographic investigation in absolute ethyl alcohol, 67.
Cadmium ion, detection by fractional method, 255.
Calcium, determination in presence of magnesium, using murexide as indicator, 221.
Carbon, New method of detecting, by heating with ammonium chloride and potassium or sodium metal, 115.
— Hydrogen and silicon, simultaneous determination in organo-silicon compounds, 225.
Carbon monoxide, separation from hydrogen, methane, by a chromathermographic method, 161.
Cell, for counter-current distribution apparatus, 697.
Cementation, of certain metals, by zinc amalgam, 331.
Cerium, effect of iron on the colorimetric determination of, 439.
Chlorex, see ether, β-β'-dichlorodiethyl.
Chlorine, new method for the specific determination of, using nitrophenol, 495.
Chlorites, determination in presence hypochlorites, using a combined iodometric and potentiometric method, 477.
Chromathermographic analysis. A chromathermographic method of separating hydrogen, carbon monoxide, methane and mixtures of inert gases, 161.
Chromatographic analysis. Accuracy of the ion-exchange method of standardizing alkali, 97.
— An absorption-precipitation chromatographic technique for the separation of nickel and cobalt by means of dimethylglyoxime, 459.
— Chromatographic separation of Ni^{2+} and Co^{2+} ions, 645.
— Chromatographic separation of radio-elements of the yttrium group of elements obtained during fission of ytterbium and hafnium by high energy protons, 605.
— Detection of traces of nickel by means of precipitation chromatography, 173.
— Determination of monoethanolamine, diethanolamine and triethanolamine in their mixtures by partition chromatography, 793.
— Precipitation chromatography in quantitative analysis, 169.
— Separation of magnesium, aluminum, chromium, manganese, iron, nickel and copper by an ion-exchange method, 285.
— The chromatographic method in qualitative analysis. Analysis of As^{3+}, Sb^{3+} and Sn^{2+}, 93.
— The use of chromatography in qualitative analysis, (detection of manganese in presence of chromium, micro-analytical detection of cobalt), 365.
Chromium, determination in steels not containing vanadium, by bismuthate method, 811.
— Separation by an ion-exchange method, 285.
Chromium alloys, see alloys.
Chromophore theory, specific character of the electronic absorption spectra of molecules, 29.
Cobalt. Amperometric titration with potassium tetrathiocyanatomercuriate, 761.
— Color reaction with β-naphthoxyquinoline for macro- and microchemical detection, 743.

Cobalt. Detection in presence of other metals, 365.
— Fractional detection of, interference by other substances, 369.
— Separation from nickel by means of an absorption-precipitation chromatographic technique using dimethylglyoxime, 459.
— Divalent, new color reaction for, using glycerol and concentrated NaOH, 813.
Co^{2+} and Ni^{2+} ions, chromatographic separation of, 645.
Colorimetric analysis. A new color reaction for divalent cobalt, 813.
— A new method for the specific determination of chlorine, 495.
— Application of trihydroxyfluorone derivatives in colorimetric analysis. Determination of antimony, 599.
— Chromotropic azo dyes as reagents for trivalent thallium, 313.
— Colored absorption reactions of magnesium hydroxide, 79.
— Colorimetric determination of beryllium by means of a new reagent — Derillon II, 417.
— Colorimetric determination of niobium and tantalum in ores, 591.
— Colorimetric determination of pyridine in air, 687.
— Colorimetric determination of sulfide ions by the molybdenum-thiocyanate reaction, 517.
— Colorimetric determination of traces of copper in metallic nickel and its compounds in the ultra-violet, 293.
— Colorimetric methods of determining small amounts of thallium 623.
— Conference on spectrophotometric and colorimetric analysis, Moscow, December 1955, 261.
— Determination of very small amounts of nitrate, nitrite and hydroxylamine, 775.
— Maintenance of temperature conditions during photo-colorimetric determination of sodium by means of NaNi $(UO_2)_3(CH_3COO)_9\cdot 6H_2O$, 25.
— New reagents for the colorimetric determination of beryllium — Berillon I and II, 409.
— Photometric and colorimetric determination of thallium as the hydroxide of trivalent thallium, 251.
— The effect of iron on the colorimetric determination of cerium, 439.
Committee, Analytical Chemistry, at the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, 124.
Complexones, new. Parafuchsinhexaacetic acid, synthesis, characterization, complex-forming and indicator properties, 423.
Conductometric analysis. Determination of ammonium by conductometric titration, 239.
Conductometric analysis. High-frequency argentometric titration, (chloride, bromide, iodide, thiocyanate and ferricyanide), 661.
Conference. first, All-Union, on the use of organic reagents in analytical chemistry, to be held on 27th and 30th November, 1956, 695.
— held in Gorky State University on the application of labeled atoms in chemistry, (Dec. 1955), 381.
— on spectrophotometric and colorimetric analysis. Moscow, December 1955, 261.
— on the application of physicochemical methods of analysis and organic reagents for control in the metallurgical and metal working industries, 693.
Congress, International, on Analytical Chemistry, Lisbon, (1956), 123.
Copper. Amperometric titration with potassium tetrathiocyanatomercuriate, 761.
— Colorimetric determination of traces in nickel and its compounds in the ultra-violet, 293.
— Method of concentrating traces of, with organic reagents (8-hydroxyquinoline, diethyldithiocarbamate), 343.
— New semi-micro gravimetric method for the determination of, using β-hydroxynaphthoic aldehyde, 309.
— Potentiometric determination with nickel diethyldithiophosphate, 559.
— Separation by an ion-exchange method, 285.
Coprecipitation, of bismuth, determination of small amounts of bismuth in Cr-Ni alloys, 733.
Corundum, synthetic, spectrographic determination of silicon and lead in powder used for the production of, 139.
Cresols, high frequency titration of, 143.
Cryoscopic method. For determination of molecular weight, nomogram for calculating weight of sample to be taken, 507.
— for the quantitative determination of arenes (aromatic hydrocarbons) in petroleum oils in cyclohexane solution, 191.
Crystal formation, excitation by friction during analytical reactions, 677.
Crystallographic analysis. Microcrystalloscopic identification of barbiturates, 503.
Cyanides, color reaction for, using chloramine, anabasine and aniline, 253.

Dimedone, use in isolation and separation of a mixture of formaldehyde and acetaldehyde, 305.
Diphenylmethane, tetramethyldiamino, for detection of ferricyanides, 215.
Distillation, vacuum, in columns, manostat and receiver for, 361.

Distribution, counter-current, Design for elementary cell of a counter-current distribution apparatus, 697.
Dyestuffs chemistry. An analytical method for direct and acid azo dyes, 219.
– Chromotropic azo dyes as reagents for trivalent thallium, 313.
– Colored adsorption reactions of magnesium hydroxide, 79.
– Sorption of certain surface active dyes by sulfides during aging, 39.

Electro-analysis. Effect of temperature on the rate of electro-analysis, 471.
Electrode, Mo|MoO$_3$||BaSO$_4$, mechanism of, use in direct potentiometric determination of the sulfate ion, 655.
Electrodes. Electrochemical behavior of, during potentiometric titration with Trilon B, 725.
– solid, oscillographic polarography on, 59.
Electrolytes, diffusion of, and the polarographic method, reply to Ya. P. Gokhstein, 543.
– A reply to the preceding article by K. Micka and A. Vlcek, 547.
Electrometric analysis. Book review. Electrometric pH determinations. Theory and practice. R. G. Bates (1954), 257.
Errata, 694.
Errors, systematic and random, in chemical analysis, evaluation of, 351.
Ethane, dichloro, mixtures with chlorex, spectrographic analysis of, 641.
Ethanolamines, mono-, di-, tri-, determination in their mixtures by partition chromatography, 793.
Ether, β, β'-dichlorodiethyl, spectra and spectrophotometric determination in admixture with dichloroethane, 641.
Ethylene glycol, and monomethyl ether, quantitative determination of, by reaction with acetic anhydride in presence of anhydrous sodium acetate, 207.
Evaporation method, and its use for the determination of boron and other impurities in uranium, 7.
– Spectrographic analysis by principles and applications, 17.
Extraction methods, Hecker book review, 819.

Ferricyanides, color reactions for, with dimethylaminoantipyrine and tetramethyldiaminodiphenylmethane, 215.
Flame, arc, see arc.
Flotation, micro, method for analysis of heavy water, 271.
Fluorine, detection in minerals and ores by a trituration method, 375.
Fluorone compounds. Applications of trihydroxyfluorone derivatives in colorimetric analysis. Determination of antimony, 599.
Formaldehyde, mixture with acetaldehyde, isolation and separation with Dimedone, 305.
Fuschsin compounds. Parafuchsinhexaacetic acid, see complexones.

Gases, inert, mixtures of, chromathermographic method of separation, 161.
Germanium, photometric determination as germanovanadomolybdic acid, 749.
Glycerides, of linolenic acid, color test for presence of, in oils, 89.
Gravimetric analysis. A method for the analysis of vanadium carbides, 179.
– A new gravimetric method for the determination of the nitrite ion using Nitriton-B (o-aminoanilide of benzenesulfonic acid), 265.
– Application of β-hydroxynaphthoic aldehyde in analytical chemistry. A new semi-micro method for the determination of copper, 309.
– Simultaneous determination of carbon, hydrogen and sulfur in organic materials, 781.
– The benzoate method of aluminum determination, 101.
– The method of "in situ nascendi" reagents for determination of the alkaline earth metals, 51.

Halogen-organic compounds, simultaneous determination of carbon, hydrogen and halogens in, 391.
Halogens, new methods for the quantitative determination of, and simultaneous determination of sulfur and halogens in organic materials, 235.
High polymer chemistry. A potentiometric method of determining saponification numbers in solutions of petroleum resins, 785.
– A quantitative method of determining acrylonitrile by means of sodium sulfite, 681.
– Cation-exchange properties of phenolformaldehyde resins in relation to the type of acid group, 617.
– Polarographic determination of acrylonitrile in aqueous alcohol solutions, 317.
Hydantoin, 2-thio derivatives, as reagents for inorganic analysis, 183.
Hydrocarbons, Aromatic, cryoscopic method for the quantitative determination of, in petroleum oils in cyclohexane solution, 191.
– paraffin, C$_{12}$–C$_{16}$, determination of degree of branching by infra-red spectroscopy, 511.

Hydrogen. Carbon and silicon, simultaneous determination in organo-silicon compounds, 225.
— Separation from carbon monoxide, methane, by chromathermographic method, 161.
Hydrogen peroxide, highly sensitive reaction for, 815.
Hydroxylamine, nitrate, nitrite, determination of very small amounts of, in presence of each other, 775.
Hypochlorites, determination in presence of chlorites, in solution, using combined iodometric and potentiometric method, 477.

Indicator, new, oxine blue, synthesis, 371.
Indicators. Acid-base, for low pH values, (tropeolone derivatives), 211.
— New, chemiluminescent, Luminol (hydrazide of 3-amino violetic acid), 125.
— New, fluorescent, dimethylnaphtheirodine, (6-dimethylamino-1,2-benzophenazine), 125.
Industrial chemistry. Polarographic determination on solid electrodes of heavy metals in the air of industrial establishments, 321.
Inorganic analysis. Derivatives of rhodanine and 2-thiohydantoin as reagents for inorganic analysis, 183.
Iodides. Determination by a mercurimetric method, 339.
— Iodometric determination of, by oxidation to free iodine in acid media, and titration with thiosulfate, 807.
Ion-exchange, method, of standardizing alkali, accuracy of, 97.
Ion-exchange resins. Cation-exchange properties of phenol-formaldehyde resins in relation to the type of acid group, 617.
Iron. Effect on the colorimetric determination of cerium, 439.
— Quantitative determination in absence of other cations, by precipitation chromatography, 169.
— Quantitative determination in presence of boric acid, aluminum salts, 105.
— Separation by an ion-exchange method, 285.
Isotope chemistry. Methods of isolating carrier free radioactive isotopes. Preparation of radiochemically pure ThB and ThC, 385.

Komarovsky, Abram Semenovich, (1865-1956), obituary, 691.

Labeled atoms, in chemistry, conference held in Gorky State University, Dec. 1955, 381.
Lactose, saccharose, photocolorimetric method of determining when they are present together, 797.
Lead, detection in ores by the trituration method, 373.
Lead, spectrographic determination of, in powder used for the production of synthetic corundum, 139.
Linolenic acid glycerides, see glycerides.
Luminescence center of sodium fluoride beads activated by uranium, composition of, 1.

Magnesium. Separation by an ion-exchange method, 285.
— hydroxide, colored adsorption reactions of, 79.
Manganese. Detection in presence of chromium, by chromatography, 365.
— Separation, by an ion-exchange method, 285.
Medicinal chemistry. A simple rational design for the elementary cell of a counter-current distribution apparatus, 697.
— Derivatives of rhodanine and 2-thiohydantoin as reagents for inorganic analysis, 183.
— The analytical characteristics of the silver salts of diethyl-barbituric acid, 243.
Mercuric chloride, photo-nephelometric determination of, by means of urotropine and potassium iodide, 529.
Mercurimetric method of determining iodides, 339.
Mercurized arylamines, see amines.
Mercury. Accurate volumetric determination of small amounts of, using stilboxine, 443.
— Volumetric analysis with thiourea solutions, 465.
— Organic compounds (arylamines), microsynthesis and identification of, 73.
Metallurgical chemistry. A bismuthate method for determining chromium in steels not containing vanadium, 811.
— Cementation of certain metals by zinc amalgam, 331.
— Colorimetric determination of traces of copper in metallic nickel and its compounds in the ultra-violet, 293.
— Color reactions for detecting cobalt and bismuth, 743.
— Conference on the application of physicochemical methods of analysis and organic reagents for control in the metallurgical and metal working industries, 693.
— Detection of lead in ores by the trituration method, 373.
— Detection of traces of nickel by means of precipitation chromatography, 173.
— Organic coprecipitants (collectors). Coprecipitation of bismuth. Determination of small amounts of bismuth in alloys based on Cr and Ni, 733.
— Separation of beryllium from aluminum and other elements by an extraction method, 405.

Metallurgical chemistry. Separation of magnesium, aluminum, chromium, manganese, iron, nickel and copper by an ion-exchange method, 285.
— Separation of niobium, tantalum and titanium by extraction, 277.
— Some properties of di-β-naphthylthiocarbazone and its bismuth and nickel complexes, 737.
— The benzoate method of aluminum determination, 101.
— The composition of the luminescence center of sodium fluroide beads activated by uranium, 1.
— The evaporation method and its use for the determination of boron and other impurities in uranium, 7.
Metals. Alkaline earth, determination by "in situ nascendi" reagents, 51.
— Cementation by zinc amalgam, 331.
— Heavy, polarographic determination of, on solid electrodes, in the air of industrial establishments, 321.
— Precipitated by dibromohydroxyquinoline, in acid solution, vanadometric determination of, 611.
Methane, separation from hydrogen, carbon monoxide, by chromathermographic method, 161.
Microanalysis. A microflotation method of analyzing heavy water, 271.
— Determination of small amounts of alkoxy groups in silico-organic compounds, 653.
— Photocolorimetric method of determining lactose and saccharose when they are present together, 797.
— Rapid method of micro elemental analysis. Simultaneous determination of carbon, hydrogen and silicon in organo-silicon compounds, 225.
— Rapid methods of micro elemental analysis. Simultaneous determination of carbon, hydrogen and halogens in halogen-containing organic compounds, 391.
— Rapid methods of micro-elemental analysis. Simultaneous determination of carbon, hydrogen, silicon and halides, 299.
— Semi micro-quantitative method for the individual determination of the higher normal fatty acids by distillation of their methyl esters, 195.
— The polarographic catalytic current of molybdenum and its use for determining microgram amounts of molybdenum, 581.
Microchemistry. Microsynthesis and identification of some mercurized arylamines, 73.
Mineralogical chemistry. Colorimetric determination of niobium and tantalum in ores, 591.
— Color reactions for detecting cobalt and bismuth, 743.
Mineralogical chemistry. Detection of beryllium when no precious metal vessels are available, 111.
— Detection of fluorine in minerals and ores by a trituration method, 375.
— Effect of the bulk composition of a mineral on results of the quantitative determination of molybdenum in granitoids, 429.
— Quantitative determination of boric acid, iron, aluminum salts, when all are present simultaneously, 105.
— Spectrochemical determination of small amounts of vanadium in samples of complex composition, 765.
— Spectrographic determination of sodium and potassium in silicate rocks, 667.
— The use of phytic acid in the analytical chemistry of thorium, 705.
Molecular weight, nomogram for calculating the weight of sample to take for determining molecular weight cryoscopically, 507.
Molybdenum. determination of small amounts of, by a kinetic method, 327.
— Effect of the bulk composition of a mineral on results of the quantitative determination of, in granitoids, 429.
— Quantitative determination in micro-gram amounts by means of its polarographic catalytic current, 581.
Murexide, preparation, use as indicator, for triolonometric determination of calcium in presence of magnesium, 221.

Naphthalene compounds. Some properties of di-β-naphthylthiocarbazone and its bismuth and nickel complexes, 737.
Nephelometric analysis. Photo-nephelometric determination of mercuric chloride by means of urotropine and potassium iodide, 529.
Nickel. Detection of traces by precipitation chromatography, 173.
— Separation by an ion-exchange method, 285.
— Separation from cobalt by means of an absorption-precipitation chromatographic technique using dimethylgyoxime, 459.
— and its compounds, colorimetric determination of copper in, in the ultra-violet, 293.
— Alloys, see alloys.
— Complex, of di-β-naphthylthiocarbazone, see thiocarbazone, di-β-naphthyl.
Ni^{2+} and Co^{2+} ions, chromatographic separation of, 645.
Niobium, colorimetric determination in ores, using pyrocatechol or pyrogallol, 591.

Niobium. Polarographic study of the electrode reduction of, in sulfuric acid solutions, 147.
— Separation from tantalum and titanium by extraction, 277.
Nitrate, nitrite, hydroxylamine, determination of very small amounts of, in presence of each other, 775.
Nitrite, nitrate, hydroxylamine, determination of very small amounts of, in presence of each other, 775.
— ion, new gravimetric method for the determination of, using Nitriton-B (o-aminoanilide of benzenesulfonic acid), 265.
Nitriton-B, see acid, benzenesulfonic, o-aminoanilide of.
Nitrophenol, as reagent for the specific determination of chlorine, 495.
Nomenclature, chemical, commission of the division of Chemical Sciences of the Academy of Sciences of the USSR, 555.
Nomogram, for calculating the weight of sample to take for determining molecular weight cryoscopically, 507.
Oils, color reaction with picric acid for detection of linolenic acid glycerides in, 89.
Ores. Detection of fluorine in, by a trituration method, 375.
— Detection of lead in, by the trituration method, 373.
Organic compounds, chlorinated, spectra and spectrophotometric analysis of. Determination of chlorex in admixture with dichloroethane, 641.
Oscillographic polarography, see polarographic analysis.
Oxine blue, see indicators.
Palladium, polarographic determination on solid electrodes, 755.
Permanganate ion, polarographic reduction on platinum and mercury electrodes, 769.
Petroleum chemistry. A chromathermographic method of separating hydrogen, carbon monoxide, methane and mixtures of inert gases, 161.
— A cryoscopic method for the quantitative determination of arenes (aromatic hydrocarbons) in petroleum oils in cyclohexane solution, 191.
— A potentiometric method of determining saponification numbers in solutions of petroleum resins, 785.
Pharmaceutical chemistry. Potentiometric investigation of barbiturates. Effect of pH on complex formation of barbiturates with the silver ion, 491.
Pharmaceutical chemistry. The dichromate method of determining piperazine, 367.
Phenol, high frequency titration of, 143.
Phenylhydrazine, 2,4-dinitro, use in amperometric titration of aldehydes, 483.
Phosphoric acids, dialkyl- and diaryldithio, use as analytical reagents, 559.
Photo-Colorimetric analysis. Photocolorimetric micro method of determining lactose and saccharose when they are present together, 797.
Photographic chemistry. A highly sensitive reaction for hydrogen peroxide, 815.
Photometric analysis. Photometric and colorimetric determinination of thallium as the hydroxide of trivalent thallium, 251.
pH values, low, new acid-base indicators for, (tropeolone derivatives), 211.
Phytic acid, use as precipitant in the quantitative determination of thorium, in monazite concentrates, 705.
Picric acid, for detection of organic compounds (linolenic acid glycerides, geraniol, tetrabutenediol, ionone, methylionone, ergosterol, carotinoids), 89.
Piperazine, quantitative determination as the dichromate, 367.
Plastics chemistry. High frequency titration, analytical control in the production of plastics, 143.
Platinum, polarographic determination on solid electrodes, 63.
Polarographic analysis. Amperometric titration of aldehyde with 2,4-dinitrophenylhydrazine, 483.
— Diffusion of electrolytes and the polarographic method. A reply to the preceding article by K. Micka and A. Vlcek, 547.
— Diffusion of electrolytes and the polarographic method, reply to Ya. P. Gokhstein, 543.
— Oscillographic polarography on solid electrodes, 59.
— Polarographic determination of acrylonitrile in aqueous alcohol solutions, 317.
— Polarographic determination of palladium on solid electrodes, 755.
— Polarographic determination of platinum on solid electrodes, 63.
— Polarographic determination of selenium, 637.
— Polarographic investigation of the chloride, bromide and thiocyanate complexes of cadmium in absolute ethyl alcohol, 67.
— Polarographic determination on solid electrodes of heavy metals in the air of industrial establishments, 321.

Polarographic analysis. Polarographic reduction of the permanganate ion on platinum and mercury electrodes, 769.
— Polarographic study of the electrode reduction of niobium and titanium in sulfuric acid solutions, 147.
— Some remarks apropos the work of I. I. Tsapiv on oscillographic polarography, 817.
— The polarographic catalytic current of molybdenum and its use for determining micro-gram amounts of molybdenum, 58.
Potassium, spectrographic determination in silicate rocks, 667.
— Tetraborate, preparation properties, use as a primary standard in acidimetry, 715.
Potentiometric analysis. Analysis of hypochlorites and chlorites in solution, 477.
— A potentiometric method of determining saponification numbers in solutions of petroleum resins, 785.
— Determination of small amounts of acids and water in polyorganosiloxane compounds, 487.
— Direct potentiometric titration of the sulfate ion using the $Mo|MoO_3||BaSO_4$ indicator electrode, 655.
— Electrochemical behavior of electrodes during potentiometric titration with Trilon B, 725.
— Potentiometric determination of copper by means of nickel diethyldithiophosphate, 559.
— Potentiometric investigation of barbiturates. Effect of pH on complex formation of barbiturates with the silver ion, 491.
— Potentiometric investigations on barbiturates. The analytical characteristics of diethyl-barbituric acid (Veronal), 243.
Przhevalsky, Evgeny Stepanovich, obituary, 823.
Pumice, silvered, use in gravimetric determination of sulfur in organic compounds, 781.
Purpuric acid, ammonium salt, see Murexide.
Pyridine, colorimetric determination in air, using bromothiocyanate reagent and aniline, 687.
Pyrocatechol, for separation of niobium, tantalum and titanium by extraction, 277.
Pyrophosphates, copper, nickel, solubility in sodium pyrophosphate solutions, instablility constants of pyrophosphate complexes, 573.

Qualitative analysis. A color test for the presence of linolenic acid glycerides in oils and a color test for certain organic compounds with picric acid, 89.
— A highly sensitive reaction for hydrogen peroxide, 815.
— Analytical applications of the formation of hexanitrohydrazobenzene, 87.
Qualitative analysis. A new color reaction for divalent cobalt, 813.
— A new method of detecting carbon, 115.
— Color reactions for detecting cobalt and bismuth, 743.
— Color reactions for ferricyanides with dimethylaminoantipyrine and tetramethyldiaminodiphenylmethane, 215.
— Detection of beryllium when no precious metal vessels are available, 111.
— Identification of solid organic binary systems by means of the melting points of the eutectics, 683.
— Microsynthesis and identification of some mercurized arylamines, 73.
— The chromatographic method in qualitative analysis. Analysis of As^{3+}, Sb^{3+} and Sn^{2+}, 93.
Quantitative analysis. Kinetic methods of quantitative analysis. Determination of small amounts of molybdenum, 327.
— Precipitation chromatography in quantitative analysis, 169.
— Quantitative determination of boric acid, iron, aluminum salts when all are present simultaneously, 105.
Quinoline compounds. Vanadometric determination of 5,7-dibromohydroxyquinoline and dibromohydroxyquinolates, 611.

Radioactive chemicals. Chromatographic separation of radioelements of the yttrium group of elements obtained during fission of ytterbium and hafnium by high energy protons, 605.
— Some questions relating to the technique of radiochemical experiments, 629.
Radioactive elements, short-lived, express drop-desorption method for the separation and identification of, 399.
Radiochemical analysis. A new apparatus for the falling-drop method of isotopic analysis of water, 803.
— Isolation and separation of a mixture of formaldehyde and acetaldehyde by means of Dimedone, 305.
Reagents, "in situ nascendi", for determination of alkaline earth metals, 51.
— new. Gallion IREA, a new highly sensitive organic reagent for the colorimetric determination of gallium, 695.
Resins, ion-exchange, see ion-exchange.
Resins, petroleum, see petroleum chemistry.
Rhodanine derivatives, as reagents for inorganic analysis, 183.

Saccharose, lactose, photocolorimetric method of determining when they are present together, 797.
Saponification numbers, of petroleum resins, potentiometric method for determination of, 785.
Selenite, uranyl, see uranyl selenite.
Selenium, polarographic determination of, as the seleno-sulfate ion, 637.
Silicates. Spectrographic determination of lithium, rubidium, and cesium in, using an improved method of introducing test samples into the arc flame, 675.
— Spectrographic determination of sodium and potassium in silicate rocks, 667.
Silicon. Spectrographic determination of, in powder used for the production of synthetic corundum, 139.
— Carbon and hydrogen, simultaneous determination in organo-silicon compounds, 225.
Silicon organic compounds. Determination of small amounts of acids and water in polyorganosiloxane compounds, 487.
— Determination of small amounts of alkoxy groups in silico-organic compounds, 653.
— Simultaneous determination of carbon, hydrogen and silicon in, 225.
— Simultaneous determination of carbon, hydrogen silicon and halides in, 299.
Silvered pumice, see pumice.
Sodium. Photo-colorimetric determination by means of $NaNi(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$, maintenance of temperature conditions, 25.
— Spectrographic determination in silicate rocks, 667.
— Fluoride beads, activated by uranium, composition of luminescence center of, 1.
Solubility products, of arsenates, 565.
Spectrographic analysis. An improved method of introducing test samples into the arc flame when working with an activated A. C. arc, 675.
— Colorimetric determination of traces of copper in metallic nickel and its compounds in the ultra-violet, 293.
— Conference on spectrophotometric and colorimetric methods of analysis, Moscow, December 1955, 261.
— Determination of the degree of branching of C_{11}–C_{16} paraffin hydrocarbons by infra-red spectroscopy, 511.
— Effect of bulk composition on the entry of individual test elements into the arc flame, 133.
Spectrographic analysis. Effect of the bulk composition of a mineral on results of the quantitative determination of molybdenum in granitoids, 429.
— New spectrographic method of analysis and its application to the determination of boron and other impurities in uranium, 7.
— Photometric determination of germanium as germanovanadomolybdic acid, 749.
— Spectra and spectrophotometric analysis of chlorinated organic compounds. Determination of chlorex in admixture with dichloroethane, 641.
— Spectrochemical determination of small amounts of vanadium in samples of complex composition, 765.
— Spectrographic analysis by the evaporation method. Principles of the method of evaporation of impurities in a vacuum and some of its applications, 17.
— Spectrographic determination of silicon and lead in powder used for the production of synthetic corundum, 139.
— Spectrographic determination of sodium and potassium in silicate rocks, 667.
— Spectrophotometric study of aqueous solutions of quinquevalent vanadium, 719.
— Spectrum analysis by means of lines located in different regions of the spectrum — method and theoretical basis, 127.
— The specific character of the electronic absorption spectra of molecules (the chromophore theory), 29.
Steels, not containing vanadium, bismuthate method for determination of chromium in, 811.
Stilboxine, synthesis, use in volumetric determination of small amounts of mercury, 443.
Strontium oxalate, precipitability in the presence of other ions, solubility in aqueous potassium nitrate solutions, 347.
Sulfate ion, direct potentiometric titration using the $Mo\,|\,MoO_3\,||\,BaSO_4$ electrode, 655.
Sulfide ions, colorimetric determination by the molybdenum-thiocyanate reaction, 517.
Sulfides, sorption of certain surface active dyes by, during aging, 39.
Sulfur, and halogens, simultaneous determination in organic materials, 235.
— gravimetric determination in organic compounds in presence of silvered pumice, 781.
Surface active dyes (neutral red), sorption by sulfides during aging, 39.

Systems, organic binary, solid, identification by means of the melting points of the eutectics, 683.

Tantalum. Colorimetric determination in ores, using pyrocatechol or pyrogallol, 591.
— Separation from niobium and titanium by extraction, 277.
Temperature, effect on the rate of electro-analysis, 471.
Thallium. Colorimetric method for determination of small amounts of, using brilliant green, 623.
— Photometric and colorimetric determination of, as the hydroxide of trivalent thallium, 251.
— Trivalent, chromotropic azo dyes as reagents for, 313.
Thiocarbazone, di - β -naphthyl, and its bismuth and nickel complexes, properties of (absorption curves, dissociation and extraction constants), 737.
Thiourea solutions, use in volumetric analysis (thiocarbamidometry), 465.
Thorium, quantitative determination in monazite concentrates using phytic acid, 705.
Thorium B and C, radiochemically pure, preparation, 385.
Tin, qualitative chromatographic method for, in presence of antimony and arsenic, 93.
Titanium. Polarographic study of the electrode reduction of, in sulfuric acid solutions, 147.
— Separation from niobium and tantalum by extraction, 277.
Titration, high frequency, see volumetric analysis.
Trilon B. Electrochemical behavior of electrodes during potentiometric titration with, 725.
— use in separation of beryllium from aluminum and other elements, 405.
Tropeolone derivatives, acid-base indicators for low pH values, 211.

Uranium. Determination of boron and other impurities in, by the evaporation method, 7.
— Determination on basis of luminescence of sodium fluride beads, composition of luminescence center, 1.
— Compounds. Maintenance of temperature conditions during photo-colorimetric determination of sodium by means of $NaNi(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$, 25.
Uranyl selenite, composition of, volumetric method for determining uranium, based on iodometric titration of liberated selenious acid, 525.
Urotropine and potassium iodide, for photo-nephelometric determination of mercuric chloride, 529.

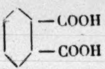
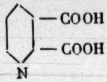
Vanadium, quinquevalent, spectrophotometric study of aqueous solutions of, 719.
— Spectrochemical determination of small amounts of, in samples of complex composition, 765.
Vanadium carbides, method for the analysis of, 179.
Vanadometric determination, of 5,7-dibromohydroxyquinoline and dibromohydroxyquinolates, 611.
Vasilev, Aleksei Mikhailovich (1882-1956), obituary, 551.
Veronal, see barbituric acid, diethyl.
Volumetric analysis. Accurate volumetric determination of gamma amounts of mercury, 443.
— A mercurimetric method of determining iodides, 339.
— A method for the analysis of vanadium carbides, 179.
— High frequency titration. Analytical control in the production of plastics, 143.
— High frequency titration. A Q-metric analytical method, 153.
— Iodometric determination of iodides, 807.
— Potassium tetraborate as a primary standard in acidimetry, 715.
— The composition of uranyl selenite. A volumetric method for determining uranium, 525.
— The use of thiourea solutions in volumetric analysis (thiocarbamidometry), 465.
— Titrimetric determination of aliphatic and aromatic amines with sodium tetraphenylboron, 789.
— Vanadometric determination of 5,7-dibromohydroxyquinoline and dibromohydroxyquinolates, 611.

Water. Determination in polyorganosiloxane compounds, 487.
— new apparatus for the falling-drop method of isotopic analysis of, 803.
Water, heavy, microflotation method of analysis, 271.

Yttrium group of elements, obtained during fission of ytterbium and hafnium by high energy protons, chromatographic separation of radioelements of, 605.

Zinc, amperometric titration with potassium tetrathiocyanatomercuriate, 761.

ERRATA

page	line	what was printed	what should have been printed
		No. 5	
601	Eq (2)	$K = \frac{x}{(1-x^2)}$	$K = \frac{x}{(1-x)^2}$
613	11		
615	5	$Mo_2O_2(C_9H_4OHBr_2)_2$	$MoO_2(C_9H_4ONBr_2)_2$
		No. 6	
726	Fig. 1	φH	φ
726	"	−0.18 − 0.20 − 0.22 − 0.24 log i mA/cm^2	−0.44 − 0.46 − 0.48 − 0.50 log i μA/cm^2

BLANK
PAGE

SECTIONS

Page

Table of Contents, 1956 1
Author Index, 1956 13
Subject Index, 1956 19
Errata i

Any of the articles listed herein may be purchased separately, exactly as they appear in the published translation, for $7.50. Individual issues may be purchased for $ 20.00 each. The price of the translation of the entire volume is $ 80.00.

When ordering articles, please cite the pagination of the English translation. Direct your orders to:

CONSULTANTS BUREAU, INC.

227 West 17th Street

New York 11, N. Y.

BLANK
PAGE

THE COMPOSITION OF THE LUMINESCENCE CENTER OF SODIUM FLUORIDE BEADS ACTIVATED BY URANIUM

T. S. Dobrolyubskaya

The Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, Moscow

Determination of small amounts of uranium on the basis of the luminescence of sodium fluoride beads, is finding, at present, wide practical application.

Despite the fact that this method has already been in use for twenty years [1], the problem of the composition of the luminescence center of the bead, is still unsolved. We define the luminescence center as a complex formation, consisting of an uranium atom and the lattice surrounding it, in which a process occurs which leads to luminescence.

Several hypotheses have been advanced in earlier papers, regarding the composition of the bead's luminescence center; these hypotheses were based on the formation of various uranium compounds such as: UF_6 [2, 3], the double salt – sodium uranyl fluoride $mNaF \cdot nUO_2F_2$ [2], and uranyl fluoride – UO_2F_2 [4].

Since sodium fluoride beads are products of reactions between sodium fluoride and uranium compounds in the molten state, it was essential, for the solution of this problem, to study and compare the luminescence spectra of the beads, and also those of all other uranium compounds which could be formed as a result of this reaction. In addition to those mentioned above, sodium uranate is also a possible reaction product [4].

Beads are normally prepared in an oxidative atmosphere; as a result, uranium compounds in which the uranium is in a lower valency state than U^{6+}, e.g. as in UF_4, cannot be formed.

Beads were prepared by a method suggested by F. Hernegger and B. Karlik [1].

Luminescence spectra of beads with varying uranium concentrations, which were photographed with a FIAN photoelectric set-up are shown in Fig. 1.

A study of the luminescence spectra showed that the shape of the spectrum is independent of uranium concentration in a bead. The form of the spectrum is maintained the same for a bead with an uranium concentration of $1 \cdot 10^{-6}$ g U/g NaF, corresponding to 1 g ion of uranium per 5,650,000 moles of sodium fluoride, and for a bead with a ratio of 1 : 1. Neither has the composition of the activating salt any effect on the luminescence spectra of the beads. The following compounds were used as activators for sodium fluoride: uranyl nitrate, sodium diuranate, uranyl fluoride, zinc oxide, and uranium tetrafluoride (uranium concentration in a bead – $5 \cdot 10^{-5}$ g U/g NaF).

On the basis of these results, it was established that the composition of the luminescence center of a bead does not change with changes in uranium concentration, and is also independent of the chemical composition of activating salt. With the aim of explaining the linear structure of the luminescence spectra, most of the subsequent work was carried out at the temperature of liquid nitrogen.

For a study of luminescence spectra at low temperatures, container and beads (three beads of the same composition were used) were placed in a Dewar flask from which some of the silver had been scraped to form an observation window. Spectra were taken on isopan plates with a sensitivity of 21°/din on a Hilger spectrograph; the slit width was 0.02 mm. The position of the lines in the luminescence spectra (at low temperature) was determined visually by means of a UM-2 monochromator.

The luminescence spectra of the following are given in Fig. 2: a) $Na_2U_2O_7$; b) UO_2F_2; beads: c) LiF – U; d) KF – U.

The luminescence spectra of the following are given in Fig. 3: a) $NaUO_2F_3 \cdot 4H_2O$; b) $NaUO_2F_3$; c) NaF bead – U (1 mole of NaF for 1 g ion uranium).

Exposure time:

$Na_2U_2O_7$ – 45 minutes
UO_2F_2 – 60 " "
Bead of LiF – U – 2.5 "
Bead of KF – U – 2 "
$Na_2UO_2F_3 \cdot 4H_2O$ – 1 "
$Na_2UO_2F_3$ – 15 "
Bead of NaF – U – 30 "
Mercury spectrum – 3 seconds

Uranium concentration in the bead $5 \cdot 10^{-4}$ g U/g NaF

On lowering the temperature from room temperature to the temperature of liquid nitrogen (–190°) in the luminescence spectra of NaF-U bead it was observed that the bands narrowed, and split up into groups of narrow lines (48 lines). A redistribution of intensity was also observed, in such a way that, while maximum luminescence intensity at 20° corresponded to 555 mμ, that at –190° was 575 mμ.

The Possibility that the Luminescence Center of the Bead is Composed of Uranium Hexafluoride

Uranium hexafluoride is a very reactive material; this compound reacts vigorously with water to form uranyl fluoride. Under the conditions used for preparing beads, when moisture is always present (beads are usually prepared in a burner flame), the probability of uranium hexafluoride formation is low.

Luminescence of solid uranium hexafluoride at low temperatures was detected and studied in 1943 [5]. At room temperature, uranium hexafluoride does not luminesce. The luminescence spectrum of solid uranium hexafluoride at 70°K, for excitation by light of wave length λ 365 mμ, extends from 4050 to 4450 A; the maximum of the luminescence spectrum is located in the violet at 4220 A. Eleven irregularly arranged lines with a mean interval of ~ 215 cm^{-1} are observed in the luminescence spectrum.

Beads luminesce brightly at room temperature. The luminescence spectra of sodium fluoride beads, activated by uranium, only start at ~ 520 mμ; the mean interval between series is ~ 860 cm^{-1}.

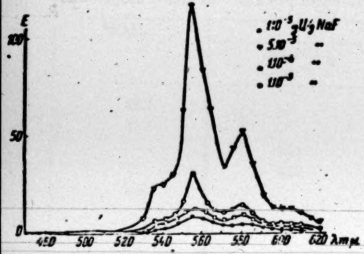
Comparison of the chemical and luminescent properties of the beads and uranium hexafluoride, led to the conclusion that this compound cannot form the luminescence center of the bead.

The Possibility that the Luminescence Center of the Bead is Composed of the Double Salt – Sodium uranyl fluoride

The presence of sodium, uranium (possibly as uranyl), and fluorine ions, is essential for the formation of the luminescence center.

This conclusion is based on the following experimental evidence: sodium fluoride on its own (without an activator), after having been fused beforehand at 1000° (Melting point of NaF is 992°), exhibits a weak blue luminescence, on excitation by light of λ 365 mμ. Activation of sodium fluoride by uranium compounds, leads to a sharp change in its luminescent properties, and to the appearance, at room temperature, of a bright yellow-green luminescence.

Fluoride ions play an important role in the luminescence of the beads. If, instead of sodium fluoride, one used other sodium salts whose melting points are similar to that of the fluoride, e.g. the sulfate, carbonate, silicate, and one prepares melts of these with zinc oxide (1%), under the same conditions as those used for preparing the melts of sodium fluoride with an uranium compound, it is found that a weak luminescence is observed in all these melts, on excitation by light λ 365 mμ; in intensity, this weak luminescence, corresponds to the luminescence of beads with uranium concentrations of ~ 10^{-5} gU/g NaF; nevertheless, in none of these melts is there observed that structure in the luminescence spectrum, which is so characteristic of the luminescence spectrum of beads (melts) of sodium fluoride activated by uranium. The sodium ion is also a component of the luminescence center. The luminescence spectra of beads, prepared from various fluorides similar in chemical properties, (NaF, LiF, and KF) and activated by uranium, differ amongst themselves.



ig. 1. Luminescence spectra of beads with
iffering uranium concentrations (Temperature
f medium + 20°).

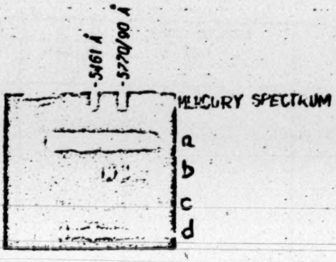
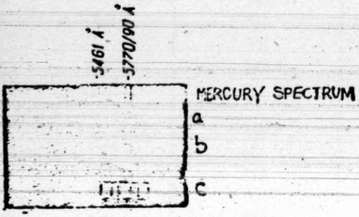


Fig. 2. Luminescence spectra at temperature of liquid nitrogen.
a) $Na_2U_2O_7$, b) UO_2F_2, c) LiF – U bead, d) KF–U bead.



ig. 3. Luminescence spectra at temperature
f liquid nitrogen.
) $NaUO_2F_3 \cdot 4H_2O$, b) $NaUO_2F_3$, c) NaF–U bead.

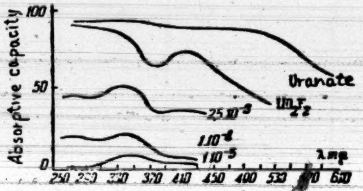


Fig. 4. Relation between absorption and uranium concentration of the bead. NaF (uranium concentration in g/g NaF).

Since the luminescence center of the beads is formed by ions of sodium, uranium (most probably as uranyl), nd fluorine, it could be that the center is composed of the double salt sodium uranyl fluoride.

At present only one double salt, with the composition – $NaUO_2F_3 \cdot 4H_2O$ is known. We prepared this salt [6] nd photographed its luminescence spectrum (at the temperature of liquid nitrogen). The most intense lines in he luminescence spectrum were the following: 497; 520.5; 545.5; 572 and 602 mμ. The luminescence spectrum f this salt was also photographed after dehydration by heating to ~ 300°. A comparison of the luminescence pectra of beads (based on sodium fluoride) and sodium uranyl fluoride, showed that the luminescence center of he beads cannot be the double salt of the composition indicated.

Ditte [6] has indicated the possibility of formation of double salts of the composition $nUO_2F_2 \cdot mMF$, where I – is an alkali metal, on fusion of uranoso-uranic oxide with alkali metal fluorides and a small amount of arbonate. Hitherto, however no salts of this type have been made. Some workers are inclined, on the whole, o think that Ditte mistakenly assumed that the uranates which are formed during this reaction were these new ompounds.

he Possibility that the Luminescence Center of the Bead is Composed of Sodium ranate

We did not manage to find any published data on the luminescence of uranates. We prepared uranates both y precipitation with $Na_2U_2O_7$, and by fusion with Na_2UO_4. At low temperatures (–190°) uranates luminesce: he luminescence spectra consists of six sharply restricted bands.

TABLE

Position of Lines in the Luminescence Spectra of Beads and Uranyl Fluoride Respectively (Temperature −190°; wave length in Tμ; concentration gU/g NaF)

UO_2F_2	NaF −U Bead			KF −U Bead	LiF −U Bead
	$UO_2(NO_3)_2$ $5\cdot10^{-5}$	UO_2F_2 $5\cdot10^{-4}$	$Na_2U_2O_7$ $5\cdot10^{-4}$	$5\cdot10^{-4}$	$5\cdot10^{-4}$
493					
497					
	511				
	512				
516					
					518
520					
522					
523					523
527					528
	530				529
	537	537	537		
540	541	541	541		
545					
547	547	547	547		
549	549	549	549		
	551	551	551		
	552.5	553	552		
				554	
				558	
	562.5	563	562	560	
567	567	568	568	566	
572	572	572	572	—	
573					
574	574	574	574		
				576	
				578.5	
				582	
	587	587	587	586	
	593.5	593	592	—	
	597.5	597	597	—	
600	601	601	601	600.5	
603	—	—	—	604	
				608	
	613	613	613	—	
	628.5	628.5	628.5		

The absence of luminescence in uranates at room temperature, and structural differences in the luminescence spectra of beads and uranates respectively, at the temperature of liquid nitrogen, rule out the possibility that the luminescence center is composed of uranates. It was shown above that the luminescence center of the beads must contain the fluoride ion.

The Possibility that the Luminescence Center of the Bead is Composed of Uranyl Fluoride

A number of factors, based on experimental evidence, indicate that uranium may possibly luminesce in the beads as uranyl fluoride: a) the structural similarity of the luminescence spectra of the beads and uranyl fluoride, respectively; b) the presence of a number of common lines in the luminescence spectra of the beads and of uranyl fluoride respectively.

We prepared uranyl fluorides by hydrolysis of uranium hexafluoride, and photographed its luminescence spectrum at the temperature of liquid nitrogen. In the luminescence spectrum of UO_2F_2 ~ 30 lines were counted; the position of the most intense lines are given in the table (these results are in good agreement with those given by Pant et al [7]).

From a comparison of the luminescence spectra of beads and uranyl fluoride respectively, it follows that there is actually much in common between the structures of these spectra; there are, however, differences in the position of the lines; some of the lines are only present in the luminescence spectra of the beads, and are absent from that of uranyl fluoride, and vice-versa. The intensity distribution between individual lines of the luminescence spectra of the beads differs from that in the uranyl fluoride spectrum.

Of the 16 lines present in the luminescence spectrum of the beads, 7 of them are observed in the luminescence spectrum of uranyl fluoride (541, 547, 549, 567, 572 and 600 mμ).

Apart from the luminescence spectra, the absorption spectra of beads, uranyl fluoride and sodium uranate were also studied. Since preparation of beads to a strictly defined uniform thickness is difficult, and it is also difficult to measure the absorption of small crystals of uranate, we measured scattering instead of absorption. Measurements were carried out at room temperature, on a FIAN set-up (E. E. Bukke). The set-up is a SF-4 spectrophotometer, in which the photo element is replaced by a photo-multiplier (readings are based on galvonometer sensitivity). The spectro-photometer was fitted with a special attachment, by means of which it is possible to place test sample and a disc of magnesium oxide and the focusing image simultaneously on the photo-multiplier. Scattering from test sample was measured with respect to scattering from a disc of magnesium oxide. Scattering from magnesium oxide was assumed to be 100 for all wave-lengths (corrections for scattering for various wave-lengths were not taken into account, since corrections have no significance for qualitative evaluation).

Absorptive capacity at a given wave-length was determined by difference: $100 - Ip = In$, where Ip — is scattering from the test sample.

In Fig. 4, are given the curves relating absorptive capacity to uranium concentration in a bead, a correction being introduced for absorption of the base — sodium fluoride. On increasing uranium concentration in the bead, absorption increases, particularly in the region 310-370 mμ.

Sodium uranate absorbs strongly, both in the ultra-violet, and in the visible. Absorption of uranate starts to decrease somewhat for wave-lengths greater than 520 mμ.

It follows from Fig. 4 that the absorption curves of the beads and uranyl fluoride are similar in shape.

Composition of the Luminescence Center of the Bead

It has been shown above that the luminescence spectra and absorption spectrum of the beads, have much in common with the luminescence spectrum (and absorption spectrum, respectively) of uranyl fluoride.

The luminescence spectrum of beads, activated by uranium, and prepared from the fluorides of the alkali metals Li, Na, and K differ amongst themselves. The cation of the basic material has an essential influence on the luminescence spectrum of the bead.

On the basis of these results, it can be concluded that the luminescence center of a bead consists of uranyl ions surrounded by fluoride and sodium ions.

The crystalline structures of sodium fluoride and uranyl fluoride have been well studied at present.

Belov [8], has shown that the oxygens in the UO_2F_2 lattice belong to the uranyl radical UO_2, and that their radii decrease sharply (at the expense of the homeopolar bond between the atoms), while, at the same time, the fluorine atoms maintain their normal radii. Sodium fluoride and UO_2F_2 form a solid solution with a limiting solubility of UO_2F_2 in sodium fluoride ($5 \cdot 10^{-5}$ g U/g NaF), while the uranyl ion occupies the position of the sodium ion in the NaF lattice. Above this concentration, uranium separates out of the melt as a new phase — sodium uranate.

A similar limited solubility of the activator was also observed in other luminescent materials, e.g. zinc sulfide, activated by copper [9].

At present, a complex flux, such as a mixture of 45.5 g Na_2CO_3, 45.5 g K_2CO_3 and 9 g NaF, is used instead of sodium fluoride for uranium determination by the luminescence method. The same lines are observed, at the temperature of liquid nitrogen, in the luminescence spectra of such a melt activated by uranium, as in the luminescence spectrum of sodium fluoride; it can be said therefore, that in this case, the composition of the luminescence center is the same as that in the bead of sodium fluoride.

I wish to thank Academician A. P. Vinogradov for suggesting this topic for study. I also wish to thank Prof. V. L. Levshin and Doctor of Technical Sciences P. N. Palei for valuable advice and attention, coworkers in the Luminescence Laboratory of the P. N. Lebedev Physical Institute for the loan of apparatus, and Academician N. V. Belov for consultations on crystallochemical questions.

Received October 31, 1955

LITERATURE CITED

[1] F. Hernegger, B. Karlik, Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt., IIa, 144, 217 (1935).

[2] M. Slattery, J. Optical Soc. Am., 19, 175 (1929).

[3] M. Slattery, Proc. Natl. Acad. Sci. U.S., 14, 777 (1928).

[4] J. Zimmerman, F. Rabbits, and E. Kornelson, Mining and Ind. Mag., 44, 54 (1954).

[5] P. Pringsheim, "Fluorescence and Phosphorescence", 1951, p. 392.

[6] D. Kats and E. Rabinovich, "Chemistry of Uranium", 1954, p. 452.

[7] D. Pant and N. Sakhwalkar, Proc. Ind. Acad., A, 19, 135 (1944).

[8] N. V. Belov, Proc. Acad. Sci. USSR, 65, 677 (1949).

[9] A. A. Cherepnev and T. S. Dobrolyubskaya, Proc. Acad. Sci. USSR, 66, 623, (1949).

THE EVAPORATION METHOD AND ITS USE FOR THE DETERMINATION OF BORON AND OTHER IMPURITIES IN URANIUM*

S. L. Mandelshtam, N. N. Semenov, and Z. M. Turovtseva

Lebedev Institute of Physics, Academy of Sciences USSR, Moscow

INTRODUCTION

The use of heavy metals presents particularly high requirements with respect to their freedom from impurities. The content of many metals should not exceed 10^{-5}-10^{-4}%. Analysis of impurities, at such concentrations, by chemical methods, is very arduous, takes a long time, and necessitates the use of large amounts of specially purified reagents. Preparation of these reagents, in turn, is a complicated and difficult problem. It is natural therefore, to turn to spectral methods of analysis for such determinations. Nevertheless, even with this technique, serious difficulties which have to be overcome, crop up. Quantitative spectral anslysis, at concentrations of the order of 10^{-5}-10^{-4}%, has not been worked out till recent years; spectro-analytical determination of impurities in heavy elements, in particular, in uranium, is connected with a number of additional specific difficulties. The bond energies of the electrons — 5f, 6d, and 7s — which participate in optical transitions, have very similar values in the atoms of the actinides; these elements have low ionization potentials and readily form oxides. This gives rise to exceedingly complicated spectra in the ultraviolet and in the visible. They form an almost continuous paling of lines, arranged on a very intense, continuous spectrum, which is determined, apparently, by the emission of solid particles of the oxides.

These characteristics of the spectra of heavy metals make it impossible to determine impurities in them with any high degree of accuracy, using the normal techniques of spectral analysis; they necessitate methods of analysis which are based on new principles**.

After long preliminary work, we became convinced that as a result of the characteristics of the uranium spectrum noted above, it is essential, in order to get the necessary sensitivity for determination of impurities, to ensure that:

a) there is complete removal, or a radical weakening of the uranium lines in the spectrum; b) the continuous spectrum is either removed or essentially weakened; c) it should be possible to use considerably more test sample for analysis than has been customary in ordinary spectro-analytical methods; d) the effect of electrode contamination should be eliminated. During our study we developed the basis of a new method, which has been called "the evaporation method"; it is described below in brief. The principles which underlie this method, appear to be the basis of a vacuum variant of the method, developed simultaneously, but independently, by A. N. Zaidel, N. I. Kaliteevsky, L. V. Lipis, and M. P. Chaika.

In the course of our investigation we became acquainted with the work of Scribner and Mullin [2], in which a method is given for the determination of 33 elements with a similar high degree of sensitivity.

Principles of the Method

The method is based on three fundamental principles:

1) the process of evaporation of test sample is separated from the spectrum excitation stage;

2) the impurities to be determined are removed from the main test element;

---

* A short description of this method was given at the Scientific Conference at Geneva (See A. P. Vinogradov "Physico-Chemical Methods of Uranium Production Control", 1955).

** Results are given in [1], which were obtained for uranium by means of the usual method — direct action of a spark on metallic electrodes. The sensitivity of the analysis, as one would expect, was 10^3-10^4 times less than that required.

3) the impurities are allowed to accumulate.

Test samples are placed in a carbon beaker which is heated, by passing an electric current through it, to the temperature at which the impurities evaporate from the samples. The vapors of these impurities condense on the surface of a special carbon or metallic receiver, arranged near the mouth of the beaker. When evaporation is complete, receiver + condensate are used as one of the electrodes in an arc or spark discharge; the discharge spectrum is registered, as usual, on a spectrograph.

This method enables one to achieve the following:

1) It becomes possible to control the fractional evaporation of test sample. By choosing the temperature to which the beaker is heated, it is possible to ensure evaporation conditions in which only impurities evaporate, since they are slightly more volatile than the base element. This ensures that the lines of the base element are removed, practically completely, from the spectrum.

Control of test sample evaporation is fairly widely used in spectral analysis — one can instance here e.g. packing the test material at various depths in the crater of the carbon electrode; regulation of heat transfer conditions by choosing the shape of the electrode; changing the current in the arc. The method we use allows the process to be controlled more accurately, and with better reproducibility.

2) It is possible to use considerably more test sample for analysis so that analytical sensitivity is increased. In our case we use weights of sample up to 2 g; when normal methods are employed, combustion is not complete if more than a few mg of sample are used. Increasing the sample weight in the apparatus normally used, as a rule, means a longer combustion time. This is accompanied by a corresponding increase in background intensity which is not conducive to an increase in sensitivity. When the evaporation method is employed, the layer of condensate formed is so thin, even when large test samples are used, that its combustion only takes a few seconds; accordingly no appreciable background is formed. The possibility of working with large samples is also advantageous, from the point of view of averaging the analytical results for heterogeneous samples.

3) By selecting the spectrum excitation source and its operating conditions, it is possible to get optimum spectrum excitation conditions for each element. In particular, during analysis of impurities which are difficult to excite, one can use a spark discharge, which one normally avoids, since it does not heat the electrodes enough for intensive evaporation of test sample, and leads to an appreciable background; when a spark is used for excitation of the thin layer of condensate, the drawbacks of the spark method are not manifested.

4) Finally, the method allows one, to an appreciable extent, to avoid the snag connected with the absence of electrode materials which are not contaminated with certain impurities. In the evaporation method, the beaker with test sample is heated to a temperature which is essentially lower than the temperature of the anode or cathode spot of the arc; accordingly, evaporation of impurities from the material of the beaker is considerably less than when carbon is used directly as the electrode; this is particularly important for determination of boron (see below).

Individual elements, used in the evaporation method, have been described in the literature. Fractional evaporation of test sample, by heating it with an independent heater, was used by Preuss, who obtained a high sensitivity for the determination of many elements [3].

Fractional evaporation of test material was also used by Scribner and Mullin; they achieved this by choosing the shape of the electrodes, combustion conditions, and by the introduction of a special "carrier". In this method, however, the stages of evaporation of test sample, spectrum excitation, and accumulation of impurities were not separated; in addition, the effect of electrode contamination was not eliminated. In particular, as a result of this, we were unable to achieve the requisite sensitivity when we tried to determine boron by their method.

A very high sensitivity was achieved for the analysis of a large number of elements, in the method of Fred, Nachtrieb, and Tomkins [4]. In their method, the test material was first dissolved, large amounts of the solution thus formed were then placed on the electrode and evaporated to give a fine film of condensate; this was finally burnt in a spark.

Finally, the processes of evaporation of test sample and spectrum excitation were separated in the work of

Rouse [5], and Shaw, Joepsuu, and Ahrens [6]; the impurity accumulation stage was omitted*.

Practical Realization of the Method

The principles of the method, as outlined above, were translated.

A good average sample of test metal, or its compounds, weighing a few grams is selected. This sample is converted into the least volatile compound of the test element, usually the oxide — by calcining. The calcined material is then well ground and an aliquot taken from it; the weight of aliquot to be taken is determined by the test conditions, and may vary from a few mg to a few g. The aliquot is introduced into a graphite beaker for evaporation. The type of beaker which we used for boron determination is depicted in Fig. 1a.

The beaker, after loading with test sample, is covered with a lid of soft graphite; it is then turned round, and evaporation is carried out from aperature "o". The attachment depicted in Fig. 2 is used for facilitating feeding of sample into the beaker. A beaker is set up in the hollow 1, and clamped in position with screw 2. Test material is strewn through funnel 5. Needle 4 is used for leaving a canal in the test sample to facilitate evaporation. A canal of this type was used by Scribner and Mullin; it proved very useful under our test conditions. Crucibles without lids, and of different dimensions, were also used for determination of other elements (Fig. 1, b, c).

Evaporation is carried out in a special evaporator. Several models were constructed; Fig. 3 depicts model IS-3. This model consists of: a main metal plate 1, two holders 2, graphite brushes 3, and a stand 4, with a holder 10. The holders 2 of the graphite brushes also serve as coolers; they are connected by rubber tubing to a water supply. One of the holders is adjustable, and can be shifted aside by means of handle 5. Beaker and test sample 6 are placed between the brushes. Uniform brush pressure is realized by means of spring 7, and can be corrected by means of screw 8 (the adjustable brush can, within certain limits, be rocked around a horizontal axis 9).

The receiver for the condensate of the evaporation products is fixed in holder 10. Vertical displacement is carried out by screw 11; horizontal displacement in two mutually perpendicular directions is also arranged for. Depending on test conditions, the receiver can be made of graphite or copper. The shape and dimensions of the graphite receiver, which we used for boron determinations are shown in Fig. 1d. The copper receivers were of similar dimensions, and had a plane front surface. Receiver is fixed in holder by friction as the result of slight taper of the latter. Water cooling is used when operating with copper receivers.

The brush holders are connected to the low voltage winding (10 V) of a 5 kW step-down transformer. The temperature to which the beaker is heated is controlled by means of a variac in the transformer primary.

Heating temperature is controlled by means of an optical pyrometer with a disappearing filament. In order that the pyrometer should not be far from the evaporator, the surface of the beaker is observed in the pyrometer by means of a plane mirror, arranged a few tens of cms behind the evaporator. The pyrometer is set to the requisite evaporation temperature beforehand; the operator then brings the temperature of the beaker up to the point at which the pyrometer filament disappears. A small correction is applied for loss by reflection. A photoelement + galvonometer were also used for controlling evaporation temperature; this method however, gave poorer results, because of the difficulty, in this case, of controlling uniform heating of the beaker.

For the sake of standardization and convenience of preparation, graphite beakers, receivers for condensates, and other graphite details were all prepared on a special machine. A few models of this machine were also made. In Fig. 4 is depicted model MS-3 **. The machine consists of a main metal plate 1, on which is fixed a headstock 2, a frame 3, and housing 4. The headstock is rotated by means of a small motor 7, via a driving belt. Interchangeable drums 5 are fitted into frame 3, and a chuck with various clamps fitted into the headstock. The graphite details are worked with a selection of chisels and drills, while details are cut out with a cutter. All graphite details are prepared from 10.5 X 10.5 mm bars. A bar is first passed through a square

---

* In the initial stages of our work, we also heated beaker + test sample with the aid of a special separate heater; spectrum excitation was carried out in an arc struck between horizontal electrodes, arranged over the beaker. This technique however, failed to give reproducible results with the requisite sensitivity.

** Engineers D. V. Emelyanov and V. F. Babaev took part in constructing the evaporator and the machine MS-3.

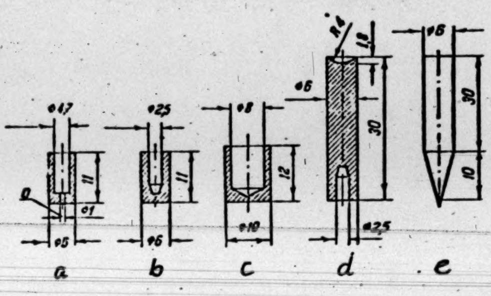

φ1,7
φ2,5
φ8
φ6
R4
1,8
φ6
11
11
12
30
30
10
0
φ1
φ5
φ6
φ10
φ2,5
a
b
c
d
e

Fig. 1. Shape and dimensions of the graphite beakers and electrodes.

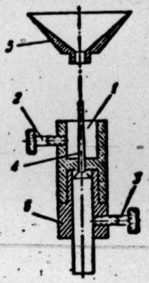


Fig. 2. Attachment for filling test sample into the graphite beakers.

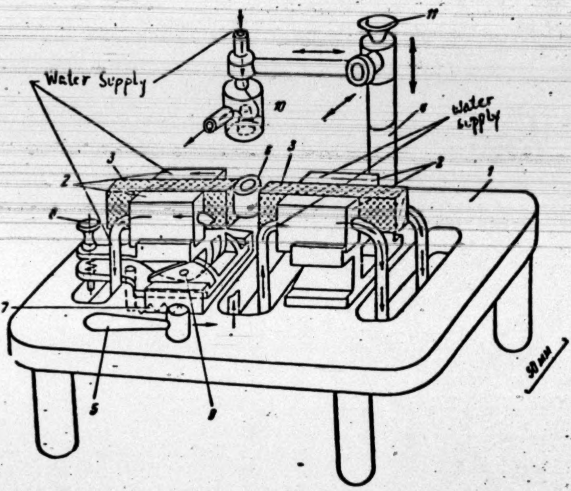

Water Supply
11
10
4
Water supply
3
2
6
3
2
1
8
7
5
9
50 mm

Fig. 3. Evaporator IS-3.

opening 9 in the drum, and turned to the requisite diameter with a chisel fixed in chuck 6. The detail is then cut out with a cutter and each detail worked with drill 11, fitted into opening 10. The drill is fed in by means of handle 12. Some of the drills are illustrated in Fig. 5. Graphite dust was removed with a dust collector (vacuum cleaner).

Condensation products are burnt either in an arc or in a spark to get the spectrum. The choice of the type of discharge to be used and its parameters, depend on the conditions encountered in a particular case, (whether the most sensitive lines of the elements to be determined belong to neutral, or ionized atoms, superposition of lines, etc.).

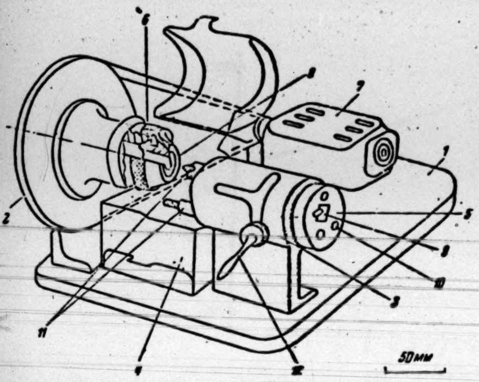


Fig. 4. The MS -3 machine for preparing graphite beakers and electrodes.

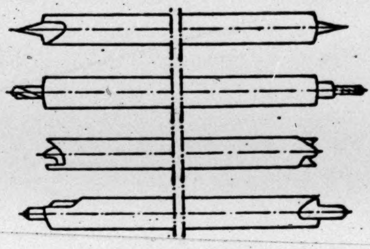


Fig. 5. Collection of drills.

Receiver + condensate are placed in the electrode holder where they serve as the lower electrode; when a graphite receiver is used, it is mounted on a tapered carbon rod fixed in a holder, for convenience of operation. Graphite or copper rods are used as the second electrode. The shape and dimensions of a graphite rod are shown in Fig. 1e.

The spectra are photographed, and the spectrograms processed as usual with standard apparatus. By means of this technique we developed a number of methods for the determination of impurities in uranium and other metals. Determinations of boron, copper, iron, nickel, and vanadium are described below.

Boron Determination

Uranoso-uranic oxide U_3O_8 was analyzed. For analysis of metallic uranium, the uranium was first converted to U_3O_8 by calcining it in an oven for 2 hours at 800°.

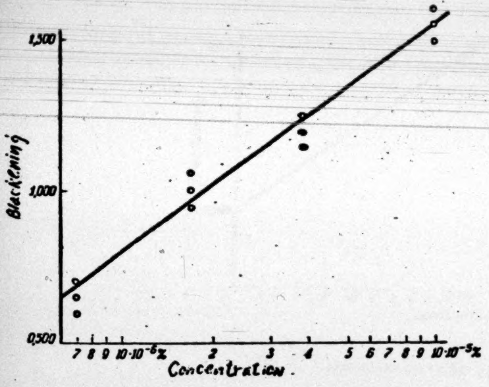


Fig. 6. Calibration curve for boron determination.

5.5-6 g of sample is taken from a test batch by quartation; this sample is then calcined in a quartz crucible in a muffle at 800° for 30 minutes. For this sample ~5 g is weighed out, and 150 mg of "carrier" added. The mixture of sample + carrier is carefully ground up in an agate mortar for 15 minutes. Addition of a carrier to the sample was suggested by Scribner and Mullin and proved effective under our test conditions also — the intensity of the boron line and of the lines of other impurities, in their spectrum, increases strongly on addition of small amounts of certain elements to the test sample. We tested the following salts as potential carriers: AgCl, Cr_2O_3, $Cr(NO_3)_3$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $CaCl_2$, $CuNO_3$, $AgNO_3$, Ag_2O, NaCl, KCl, $Cd(NO_3)_2$, $Bi(NO_3)_3$, $Pb(NO_3)_2$, $Sn(NO_3)_2$, $SnCl_2$, $Ga_2(NO_3)_3$, $Ga_2(SO_4)_3$, Ga_2O_3, $Al_2(SO_4)_3$.

Experiment showed that each carrier has its own special evaporation temperature, and has a different effect on the various elements contained in the test sample. It was established, at the same time, that if the sample contains large amounts of volatile impurities, e.g. alkali metals, these impurities themselves act as carrier, and enhance the intensity of the boron lines.

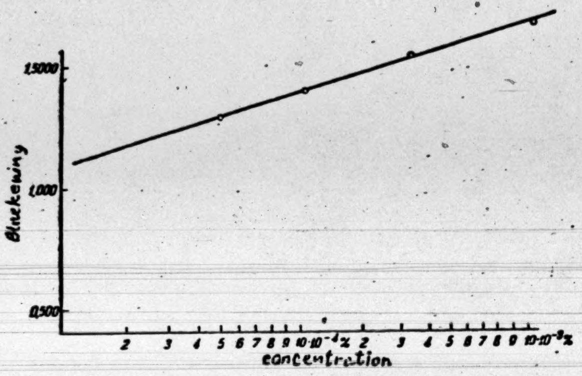


Fig. 7. Calibration curve for copper determination.

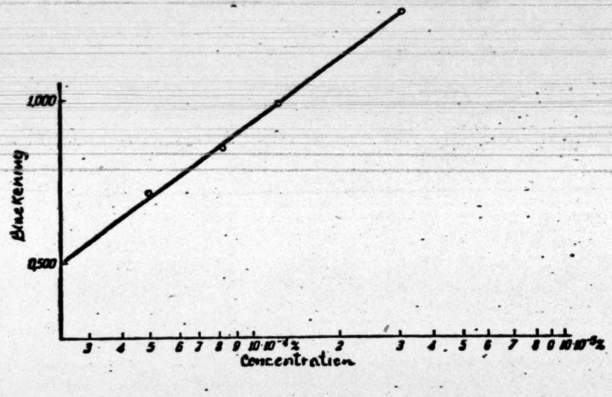


Fig. 8. Calibration curve for copper determination.

We decided on a carrier consisting of spectrally pure gallium oxide and uranoso-uranic oxide, containing not more than 1-2 · 10^{-5}% boron, in the ratio 1 : 12 (Scribner and Mullin also used gallium oxide as a carrier at a rate of 2%). In addition, experiments were carried out, in which gallium oxide was added to the condensate receiver, not to the sample to be evaporated; the surface of the receiver was sprinkled with powdered gallium oxide by means of a pulverizer. The boron lines were also strengthened when this technique was used, but the effect was unstable.

From the mixture of test sample + carrier, prepared as described above, an aliquot of 250 mg is taken. To speed up analysis we decided not to bother to weigh out each aliquot individually, but measure it out by packing to standard volume. It was established that for standard packing, with strict observance of beaker dimensions and use of the attachment used for packing depicted in Fig. 2, good reproducibility for aliquot weights was obtainable — the maximum scatter for weights of 250 mg did not exceed ∓ 10 mg, i.e. ∓4%.

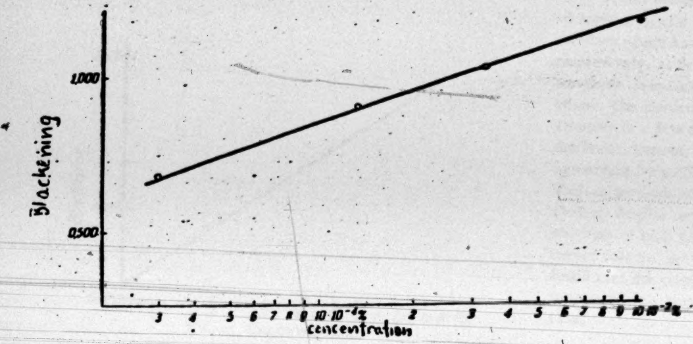


Fig. 9. Calibration curve for iron determination.

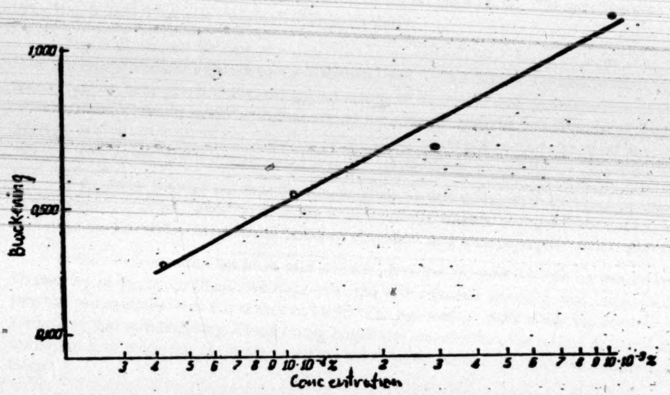


Fig. 10. Calibration curve for nickel determination.

Optimum evaporating conditions were worked out: best results were obtained on heating the beaker to 1800° for 20 seconds, and keeping the beaker at this temperature for another 20 seconds.

The shape of the surface of the condensate receivers was the subject of a special study. It was found that the most reproducible analytical results are obtained when the surface is slightly concave, as shown in Fig. 1d. This ensures complete combustion of condensate on exposing the surface to a D. C. arc. The optimum shape of the second electrode of the arc proved to be that shown in Fig. 1e. Receiver + condensate serve as the arc anode.

Four standards were used for analysis — one was a specially chosen basic material — while the others were prepared synthetically by adding boron to this material. Boron was added as a boric acid solution. The following boron standards were prepared: 1) $c = c_0$. 2) $c = c_0 + 1 \cdot 10^{-5}\%$B. 3) $c = c_0 + 3 \cdot 10^{-5}\%$B. 4) $c = c_0 + 1 \cdot 10^{-4}\%$B where c_0 — is the initial boron concentration of the base material, which was used for preparing the standards; it was determined by replicate chemical analysis, and also directly by a spectrographic method. The respective amount of carrier was added to each standard.

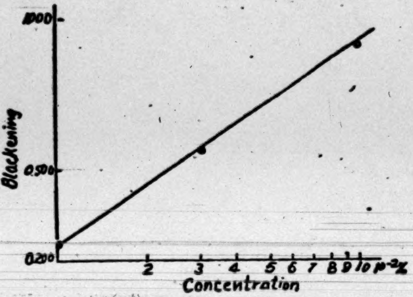


Fig. 11. Calibration curve for vanadium determination.

It was established that analysis of samples of uranoso-uranic oxide, and analysis of metallic uranium which has been converted into the oxide respectively, as described above, require separate standards, prepared on correspondingly different bases. The deviation between the two curves amounts to a few dozen percent with respect to the boron content. We tried to get a closer agreement by preliminary treatment of samples. Various methods of treatment were used: nevertheless, despite outward similarity in the structure of both types of samples, the calibration curves still did not coincide. Later, E. E. Batasheva found that the graphs will coincide, if boron is introduced into the standards as crystalline boric acid.

An ISP-22 spectrograph was used to get the spectrograms. The arc current was 10 A; exposure 6 seconds. Each sample was photographed three times (the upper electrode was left unchanged). The spectrogram of all four standards were photographed three times on each plate. The spectrograms were processed as usual. The line B 2497.77 A was measured photometrically.

Fig. 6 illustrates the type of calibration curve we obtained (boron content of base material $c_0 = 7 \cdot 10^{-6}$%). The analytical accuracy (mean of three spectra) was ~10-15% of the concentration being determined. As examples, we have given in the table, the results of chemical and spectrographic analysis (using a few plates) of several samples; the arithmetic mean error for a single analysis was calculated from the results of the spectrographic analysis of a given test sample. In several instances, a second chemical analysis was made; usually, this led to closer agreement between the results of both methods, as can be seen from the table.

It should be pointed out that the results given in this table, were obtained by means of this method, right at the beginning of our work; later, as we developed the method and got practical experience, the accuracy increased considerably. Agreement between chemical and spectrographic results also improved appreciably.

It follows from what has been said already, that the method is based on measurement of the absolute blackening of the boron lines. We experimented with relative intensity, and introduced various reference elements into the test samples with this object in view. Ga, Ag, and Cr were tried; the accuracy did not improve. Reckoning that standardizing all operating conditions ensures that the results obtained are accurate enough, while introduction of reference elements complicates matters, we did not carry out further experiments along these lines.

With respect to the sensitivity of the method, by which we mean the lowest boron content so far determined, we can state: the lowest boron content which we have tested is ~$7 \cdot 10^{-5}$%. At this concentration, blackening of the boron line amounted to 0.65. Without going beyond the limits of the straight line part of the characteristic curve of the plate, it is possible to work at considerably lower blackenings; it is also possible to increase the amount of evaporated sample. This means that the sensitivity can be made higher. It should be noted that the fundamental difficulty in spectral analysis of boron, is the impossibility of removing boron completely from graphite whatever method of purification is employed; apparently, boron remains in graphite as boron carbide. Boron carbide requires a high temperature for its decomposition; in ordinary methods, and also in Scribner and Mullin's method, such a temperature is developed at the places of contact between arc and electrode, where a temperature of 3000-3500° is reached. In the evaporation method, graphite beaker + test are only heated to 1800-2000°; at this temperature, decomposition of boron carbide does not occur. The graphite receiver on which condensation occurs, although it does come into contact with the arc, only does so for a very short time (exposure 6 seconds) at comparatively low current strengths. Accordingly, as experiment showed, the evaporation method does not require graphite of exceptionally high purity, and it does not limit the sensitivity of the method.

Determination of Copper, Iron, Nickel, and Vanadium

The method employed for these metals is very similar to that used for boron determination; accordingly, we shall only touch briefly on them.

Results of Boron Determinations in Uranium (in %)

Experi-ment number	Sample number	Results of chemical analysis X $1 \cdot 10^{-6}$	Results of a duplicate chemical analysis X $1 \cdot 10^{-6}$	Results of spectrographic analysis (X $1 \cdot 10^{-5}$) N spectrograms												Mean value X $1 \cdot 10^{-6}$	Mean arithmetic error of a single determination in %
				131	132	133	135	136	137	138	139	140	141	142	143		
1	120	2.8	3.4	4.8	6.0		5.0	5.5			4.7	5.5	4.0		6.5	5.2	11
2	123	2.7							2.7	2.6		2.4		1.7	1.7	2.2	18
3	126	1.7			1.6	1.7		1.6	2.0			2.4	2.3	1.6	1.4	1.8	17
4	206	1.6	2.2	3.0		4.1		2.7	3.5				3.0		3.5	3.3	12
5	207	1.4	2.2	2.1	3.0	2.8	2.7	2.2	2.6			2.3	2.6		2.5	2.5	10
6	210	1.2						2.6	2.7				2.3	1.8	1.8	2.2	16
7	259	1.1			1.0	1.0	1.2								1.0	1.0	5
8	269	1.1		1.6				1.5	1.7							1.6	6
9	275	1.1						0.7	1.0	0.8		1.3		0.9	1.1	1.0	14
10	416	2.5						2.7	2.7			3.0			2.3	2.7	6
11	131	5.5		5.0	6.0	5.8	6.0									5.7	6
12	161	4.8	2.2							2.4	2.2		3.0	2.4		2.5	10
13	262	3.6	3.1							3.1	3.1		3.4	2.4		3.0	10
14	280	1.8	1.8							0.7	0.9		1.4	1.0		1.0	20

Copper was determined by means of the lines Cu 3247.54 and 3273.96 A, starting at concentrations of $1 \cdot 10^{-4}$%. Fig. 7 represents the calibration curve. The slope of the graph can be increased (Fig. 8), if the amount of copper vapor in the arc is decreased. This was achieved by cutting test weights down to 30 mg, changing the shape of the beaker, (Fig. 1b), and cutting the arc current down to 5 A.

Iron was determined by means of the line Fe 3020.64 A starting at a concentration of $1 \cdot 10^{-4}$%; the calibration curve for iron is shown in Fig. 9.

Nickel was determined by means of the line Ni 3002.49 A (Fig. 10), starting at a concentration of $1 \cdot 10^{-4}$%.

Standards for all these determinations were prepared by introducing mixtures of CuO, Fe_2O_3, and Ni_2O_3 respectively with carriers, similar to those used for boron determinations, into uranoso-uranic oxide.

Vanadium was determined by means of the line V 3183.98 A, starting at a concentration of $1 \cdot 10^{-4}$%. In order to get this sensitivity, the weight of test sample had to be increased to 2 g. The graphite beaker shown in Fig. 1c was used for these analyses. In order to weaken the intensity of the continuous spectrum near the line chosen for vanadium, we used spectrographic apparatus with a longer focusing collimator (a Hilger auto-collimating spectrograph) for these analyses. Standards were prepared by introducing V_2O_5 into uranoso-uranic oxide; the curve is illustrated in Fig. 11.

The mean analytical accuracy in all the cases enumerated was about 10-15% of the actual content (results were based on three spectra).

This work was carried out during 1947-1949.

We wish to thank E. E. Batasheva, R. L. Mirogorodsky, A. P. Chekulaeva, and G. G. Chernyshev for their cooperation during the work.

SUMMARY

A new spectrographic method of analysis, and its application to the determination of boron and other impurities in uranium is described. A test sample is placed in a graphite beaker which is heated in a special evaporator to a temperature, at which evaporation of impurities occurs, with only negligible evaporation of the principal element. The evaporated impurities

condense on the surface of a special carbon or metallic receiver, and combustion is carried out in this with an arc or spark discharge. In this method therefore, the evaporation stage is isolated from the spectrum excitation stage; a new link is introduced — accumulation of impurities.

The following metals can be determined in uranium by this method: boron — starting at concentrations of $7 \cdot 10^{-6}$%; copper, iron, and nickel — starting at concentrations of $1 \cdot 10^{-4}$%; vanadium — starting at concentrations of $1 \cdot 10^{-2}$%; the sensitivity of determination of these metals can be increased. Analytical accuracy amounts to ~ . 10-15% of the determined content.

Received November 22, 1955

LITERATURE CITED

[1] A. Walsh, Spectrochim. Acta, 4, 47 (1950).

[2] B. F. Scribner and H. R. Mullin, J. Research Nat. Bur. Standards, 37, 379 (1946).

[3] E. Preuss, Z. angew. Mineral, 3, 8 (1940).

[4] M. Fred, N. Nachtrieb and F. Tomkins, J. Optical Soc. Am., 37, 279 (1947).

[5] A. Rouse, J. Optical Soc. Am., 40, 82 (1950).

[6] D. M. Shaw, O. J. Joepsuu and L. H. Ahrens, Spectrochim. Acta, 4, 233 (1950).

SPECTROGRAPHIC ANALYSIS BY THE EVAPORATION METHOD

I. PRINCIPLES OF THE METHOD OF EVAPORATION IMPURITIES IN A VACUUM, AND SOME OF ITS APPLICATIONS

A. N. Zaidel, N. I. Kaliteevsky, L. V. Lipis, M. P. Chaika, and Yu. I. Belyaev

Physical Institute of the Zhdanov State University, Leningrad, and the Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, Moscow

The purity of materials which are used in modern techniques is so high that ordinary spectrographic methods are not sensitive enough for successful production control of such materials.

One of the basic factors which limits the concentration sensitivity of spectrographic analysis (i.e. the minimum concentration of a material which can still be detected in a test), even when there is an unlimited supply of test material, is the spectrogram background; this may be caused by the continuous spectrum of the source of light, or, by a multitude of unresolved lines which belong to the principal element in the test material — if the latter possesses a complex multi-linear spectrum.

To increase analytical sensitivity it would be convenient to remove the impurities to be determined from the principal component of the test, and to subject only the separated concentrate of impurities to spectrographic analysis. When such a technique is used, the concentration sensitivity can be increased considerably (tenfold and hundred fold), if one can separate the impurities completely for a sufficiently large weight of test material.

Separation of the elements to be determined eliminates the effect of the principal component of test samples on line intensity; in many cases, this leads to an increase in sensitivity. This fact is of special importance when the principal elements of the test material happen to be elements with low ionization potentials.

Various chemical and physico-chemical enrichment methods are in use at present. All the same, chemical methods usually take a long time. Practically all chemical enrichment is accompanied by loss of the elements to be determined, or, on the other hand, by contamination of test material by reagents, during chemical enrichment operations.

Physical enrichment which would be followed up by spectrographic analysis is, therefore, a particularly attractive proposition. Such a method can be worked out if the impurities are present in the test samples as compounds whose vapor pressure, at a certain temperature, is essentially higher than that of the principal component. In such a case, it would be possible to separate the spectra of the impurities and the multi-linear spectrum of the principal component of test materials.

This principle of fractional distillation, which occurs in the light source, has been used for a fairly long time in spectrographic analysis. One can instance the work of Rusanov [1], on the determination of molybdenum in ores. In this case, use was made of the high volatility of molybdenum oxides. The analysis of uranium by Scribner and Mullin [2], is an example of the successful use of fractional distillation in spectrographic analysis.

In all these cases, where fractional distillation has been used, excitation of the spectra is effected simultaneously with evaporation of impurities from the test sample, by the same source of heat and light — a D. C. arc. The possibility of controlling the process of spectra excitation and evaporation of impurities has proved to be limited.

Rouse [3], in his work published after the basic principles and practical application of the method set out below had been worked out, went a bit further. Rouse used an independent source of heat for heating test samples — a high frequency oven.

To increase the sensitivity of halogen determinations, Levintov [4], used a variety of sources, one of which in fact, only served to heat test samples.

Complete separation of the stages of evaporation of impurities, and the excitation of their spectra is a fundamental principle of the method we have developed. Separation of these stages, opens up wide possibilities for more accurate and controlled selection of optimum conditions, for evaporation, and spectra excitation, of elements to be determined. The method is applicable in all cases where there is an appreciable difference between the vapor pressure of impurities and the principal elements of test samples. It has been called the "evaporation method". This same principle was put forward, and used, in a method for the determination of boron in uranium by S. L. Mandelshtam, N. N. Semenov, and Z. M. Turovtseva [5]. These authors evaporated the impurities under atmospheric pressure. A comparative evaluation of this type of evaporation, with evaporation in a vacuum, which we adopted, is given below.

EXPERIMENTAL

Evaporation of Impurities in a Vacuum

Initially, we used a specially constructed miniature graphite oven of the Knig type, suggested by A. N. Zaidel in 1947, for independent heating of the test samples. Later, we used a more convenient type of heater, construction of which was based on a method of heating developed in S. L. Mandelshtam's laboratory.

As a basis for separation of volatile impurities from the less volatile principal elements, evaporation in a vacuum with condensation of the vapors of the impurities on the face of a cooled copper or graphite capsule was used. These capsules served as one of the electrodes of the light source during subsequent spectrographic analysis of the condensate.

The set-up used for evaporation is a small cylindrical graphite oven 3 (Figs. 1 and 2), heated by a current from a step-down transformer. (A welding transformer is suitable for this purpose). The current is led in through contact graphite clamps 4, cooled by a condenser with flowing water. The body of the oven has a side opening 7 for observation of the temperature of the graphite beaker + test sample 2, placed in the oven. Temperature is measured with a pyrometer. Above the oven, on a folding holder cooled with water 8, the copper or graphite capsule 1 is fitted. This holder is constructed in such a way that the capsule can be fitted directly above the opening of the beaker containing test sample. The gap between beaker and capsule is 1-2 mm. Accurate adjustment of the oven between the clamps, which ensures uniform heating, is made with the aid of screw 9. The current and cooling water are led along the supports of clamps 4, which pass through insulating packing 10, through steel plate 11, serving as a base for the set-up. Vacuum is applied through tube 12. During operation the set-up is covered with a glass bell jar 13. The base 11 is fitted with a lining of vacuum rubber. The current in the transformer primary is regulated by means of an auto-transformer. The general appearance of the vacuum evaporator is shown in Fig. 4.

Evaporation of test elements from the sample is carried out as follows: 10-50 mg of sample (depending on the properties of the test material and on the sensitivity required) is placed in a graphite crucible, which, in turn, is placed in the oven. The sample is heated at a temperature of 200-600°, according to the property of the principal element, to remove adsorbed water and gases. After this preliminary heating, the capsule is placed in position, the glass bell jar is fitted in position, and the vacuum switched on. When the requisite vacuum has been attained ($< \sim 0.01$ mm Hg[*]), the current is switched on, and beaker + test material heated to the required temperature. This temperature, as noted already, is determined by the vapor pressure of the principal element, and of the impurities. It varies from 1400-2000° depending on the analytical problem to be solved. The test sample is heated for 1-2 minutes at this temperature for complete removal of volatile components. Evaporation of impurities from standards is also carried out under identical conditions.

Spectrographic Analysis of Condensate

For quantitative determination of impurities, condensed as a result of evaporation on graphite or copper capsules, the latter are used as one of the electrodes in a spark discharge. Control of the electrode set-up is realized by means of shadow projection. Usually, a single condenser lens was used for illuminating the spectrograph slit. The absence of a spectrum belonging to the principal element permits the use of spectrographs with average dispersion: in the ultraviolet — the ISP-22 or K-24 (Qu-24); in the visible — ISP-51, with a focal length of 270 mm for the camera.

---

[*] It was shown experimentally that further increases in the vacuum, did not give essentially better results, and, moreover, was connected with considerable technical difficulties.

The comparatively high light strength of these spectrographs is reflected favorably in the absolute sensitivity of the spectroscopic determinations. In certain cases it was necessary to use the KS-55 spectrograph. The spectra were sometimes photographed simultaneously with two or three spectrographs (Fig. 3).

For the photometric part of the work, we usually used the method of three standards, without attempting to use a rigid calibration curve. Photographing the spectra of test samples and standards on one plate, though it lengthens the time for an analysis somewhat, did not lead to more reliable quantitative determination of impurities.

For such an analysis, it is essential, to get reliable results, that one can be sure that the percent extraction of impurities from the principal element is constant. By carrying out preliminary work with the aid of radioactive isotopes we were able to find the best, and most stable evaporation conditions, for each concrete analytical case. The extent of the condensation* of impurities on the capsules under these optimum conditions, amounted to 85-98% (see Table 4).

Sensitivity and Accuracy of the Evaporation Method

In the method of physical enrichment, based on separation of the processes of evaporation of impurities and excitation of their spectra, the operation of evaporation is itself a preparation of the sample for analysis. After evaporation, the impurities are concentrated on the face of the graphite or copper electrode; consequently, the sensitivity of a determination by the evaporation method depends only on the absolute sensitivity of spectrographic determination during excitation of the spectra of the impurities, in some form or other of light source. When it has been shown that evaporation and condensation of test elements on the capsule is complete (i.e. 100% of impurities have evaporated and 100% condensed on the capsule) under the conditions chosen for analysis (as determined e.g. by means of radioactive indicators), then, for a given absolute sensitivity which is determined by the choice of light source, the method used for recording the spectra etc, the concentration sensitivity of the evaporation method will be determined by the size of sample taken, which can be increased considerably. This feature of the evaporation method distinguishes it essentially from the usual spectrographic methods, which are based on direct combustion of an aliquot of test material in a light source. All the same, we cannot increase sample weight indefinitely, because of increasing technical difficulties, and as a result of the fact that, in certain cases, when large weights of test samples are used, the percentage impurities evaporated falls for a given diameter and depth of the graphite beaker. In order to increase the sensitivity of a determination therefore, it is expedient to photograph the spectra of impurities for several capsules + condensates on the same place on the photographic plate. By this means one gets, apart from an increase in sensitivity, considerable neutralization of the sample.

From what has been said above, it is clear why the evaporation method is highly sensitive. The advantages of the evaporation method become very obvious when we compare the absolute analytical sensitivity of the evaporation method with the absolute sensitivity of the determination of the same elements by Scribner and Mullin's method [2], in which the phenomenon of fractional distillation in a D.C. arc is employed without any separation of the process of evaporation from that of spectrum excitation.

A comparison of these methods is given in Table 1; calculations of the absolute sensitivity of the evaporation method are based on an aliquot of 100 mg as indicated in Scribner and Mullin's method.

Under optimum evaporation conditions and for a high absolute sensitivity of spectrographic determination, the concentration sensitivity of the evaporation method is also very high.

Table 2 contains data on the concentration sensitivity of analysis by the evaporation method for impurities from compounds with low volatility.

---

* The extent of condensation of any element is determined by the ratio of the number of atoms of this element, condensed on a capsule, to the total number of atoms of this element found in the test sample before evaporation. The extent (completeness) of evaporation is determined by the ratio of the number of evaporated atoms of any element to the total number of atoms of this element before evaporation. The extent of condensation and the extent of evaporation are expressed in per cent, and are practically equal to each other, with the exception of cases noted in the text (see footnote to Table 4, p. 23).

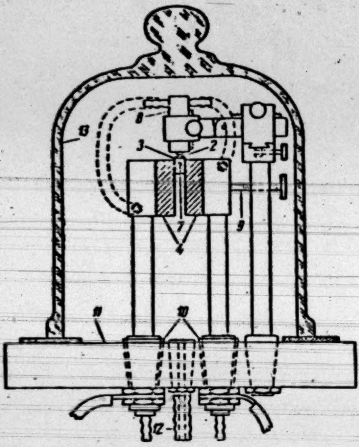


Fig. 1. Scheme for vacuum evaporator.

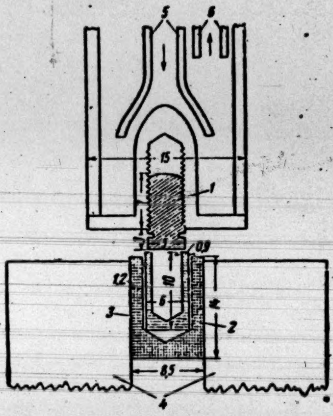


Fig. 2. The evaporation set-up.
1) cooled capsule; 2) inner graphite beaker containing test sample; 3) outer graphite beaker (oven); 4) contact graphite clamps; 5) tube for leading in water; 6) tube for carrying away water; the rubber tube for conducting the water is shown by the arrows.

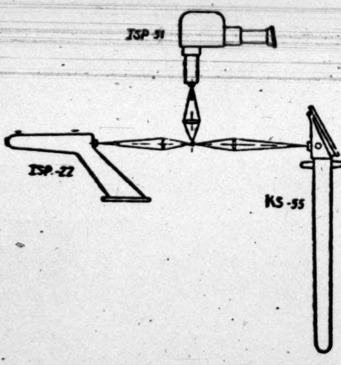


Fig. 3. Mutual arrangement of spectrographs.

It must be pointed out these results relate to cases where the impurities to be determined evaporate practically completely. Experiments carried out with the aid of radio-active indicators show that, in many cases, this actually is the case. Incomplete condensation of impurities on a capsule as a result of choosing the wrong evaporation conditions, leads, sometimes, to a considerable decrease in the sensitivity of a determination. Moreover, when analysing readily volatile elements (Cd, Zn, etc.), one must take into account the possibility that evaporation in reverse may occur, after condensation of the impurities on the face of the copper or carbon capsules; this may happen as the result of strong heating of the capsules by the adjacent incandescent graphite beaker. This effect however, disappears when cooling of capsules is efficient.

The accuracy of the evaporation method is not inferior to that of spectrographic analytical methods normally used for the determination of small concentrations of impurities. An evaluation of the reproducibility of analytical results obtained by the evaporation method, shows that the mean square error of a single determination varies within the limits of 15-20%, according to the properties of the test element.

Friable thick layers are broken up by a spark, and excitation is far from complete; this means a decrease in accuracy and sensitivity. Accordingly, the evaporation method is efficient enough, when it is used for the analysis of pure products. The presence in test material of a readily volatile impurity in amounts greater than 1%, almost reduces to nothing the advantages of this method of physical enrichment.

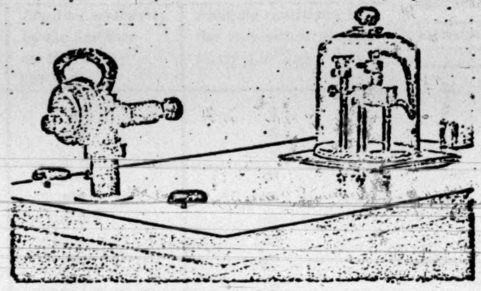


Fig. 4. General appearance of the vacuum evaporator. Pyrometer on the left.

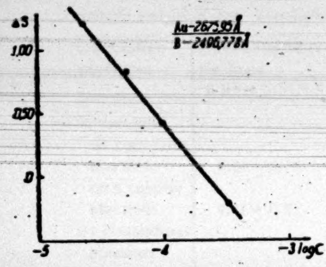


Fig. 5. Calibration curve for determination of boron by the evaporation method. Gold was used as the internal standard.

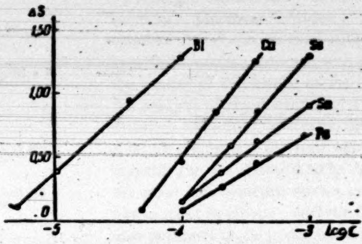


Fig. 6. Calibration curves for determination of bismuth, copper, antimony, tin, and lead in alumina by the evaporation method.

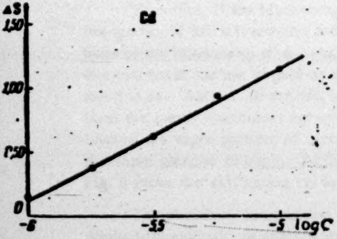


Fig. 7. Calibration curve for determination of cadmium in alumina by the evaporation method.

When impurities are evaporated in a vacuum from fairly pure test samples, a uniform and stable condensate layer is obtained on which interference rings are sometimes visible. When evaporation is carried out in air (not in a vacuum) the condensate film usually has a more friable structure, which leads to some loss of accuracy and sensitivity. Nevertheless, in those cases where the principal element is itself volatile when evaporation is carried out in a vacuum, there is no alternative to evaporation at atmospheric pressure. Results are given in Table 3 characterizing the value and scatter of the blackening of boron lines on evaporating in vacuum and at atmospheric pressure, respectively.

TABLE 1

Comparison of the Sensitivity of Analysis by the Evaporation and the Scribner-Mullin Methods Respectively

Element	Absolute sensitivity by the Scribner method in mγ (10^{-9} g)	Absolute sensitivity by the evaporation method in mγ (10^{-9} g)
Li	10	1
Mn	100	5
B	8	5
Cr	300	10
Co	100	25
Ni	200	50
Sb	1000	100
Pb	100	20
Sn	100	10
Bi	50	2
Cd	7	1

TABLE 2

Concentration Sensitivity of Analysis by the Evaporation Method.
Sample weight 50 mg

Element	Concentration sensitivity in %	Element	Concentration sensitivity in %
Li	$2 \cdot 20^{-3}$	Cd	$1 \cdot 10^{-5}$
B	$1 \cdot 10^{-5}$	Sb	$1 \cdot 10^{-4}$
Cr	$2 \cdot 10^{-5}$	Bi	$5 \cdot 10^{-6}$
Co	$5 \cdot 10^{-5}$	Pb	$5 \cdot 10^{-5}$
Mn	$2 \cdot 10^{-6}$	Sn	$5 \cdot 10^{-5}$
Ni	$1 \cdot 10^{-4}$	Cu	$5 \cdot 10^{-5}$

TABLE 3

Sample weight 50 mg. Standard $5 \cdot 10^{-5}$% boron

Evaporation conditions	Blackening corrected for background near the lines	
	S lines 2497.7 A	S lines 2496.7 A
In vacuum:		
on a graphite electrode	0.64 ± 0.02	0.52 ± 0.03
on a copper electrode	0.75 ± 0.01	0.62 ± 0.01
At atmospheric pressure:		
on a copper electrode	0.42 ± 0.12	0.30 ± 0.08

Photometric treatment of results, based on measurements of the difference in blackening between the analytical lines of test elements, and the lines of the principal element of a test sample, is left out in analysis by the evaporation method.

The reproducibility of analysis by the evaporation method can be increased considerably by adding a suitable internal standard (reference element). Moreover, addition of an internal standard allows one, in most instances, to avoid systematic errors connected with deterioration of the quality of the deposit on the capsule. During the analysis of any material for a large number of different impurities, it is often difficult to choose a suitable reference element which has a similar volatility to the elements to be determined. All the other requirements which a reference element has to meet in ordinary analytical methods are also pertinent in the given instance. It must be pointed out however, that if one succeeds in selecting an internal standard for the most important element, the systematic errors in the determination of the remaining elements decrease appreciably. This, as stated already, is bound up with the fact that the quality of the layer on the capsule affects the blackening of the lines of all the elements to be determined.

Therefore, if the blackening of the lines of the reference element remains approximately the same in all the spectra of the test samples and standards, one can, with considerable assurance, carry out an analysis on the basis of the blackening of the analytical lines. As an example of the successful choice of an internal standard, one can quote the use of gold as an internal standard in boron determinations. We added 1-2 mg of gold in solution as AuCl to the test sample. On calcining the test sample (~800°) auric chloride decomposes to form the metal which does not evaporate from the test sample at this temperature. On increasing the temperature further, the vapor pressure of metallic gold increases practically according to the same law as that which holds for the vapor pressure of boron. At 1600-1700°, both gold and boron are removed completely from the test material. Fig. 5 shows the calibration curve obtained for boron determination when gold is used as the internal standard.

The chemical composition of standards should be similar to that of test samples, as in the usual spectrographic methods of analysis, in order to cut down systematic errors.

Application of the Vacuum Evaporation Method to the Analysis of Pure Aluminum Oxide

As an illustration of what has been said in previous sections, we give below, as an example, the application of the vacuum evaporation method for determining traces of Cd, Sb, Bi, Pb, Sn, and Cu in pure Al_2O_3. Normal spectrographic methods, using a D.C. arc, gave the following sensitivity limits, when used for determining the elements indicated: Cd $\sim 10^{-3}$%, Bi $\sim 5 \cdot 10^{-4}$%, Sn $\sim 10^{-3}$%, Sb $\sim 10^{-2}$%, Pb $\sim 10^{-3}$%, Cu $\sim 5 \cdot 10^{-4}$%. Increasing the weight of sample taken, only led to an increase in spectrum background, and did not effectively increase the sensitivity. Such sensitivity, in many cases, is insufficient. Application of the vacuum evaporation method to the analysis of comparatively slightly volatile Al_2O_3, for the impurities listed, permitted a significant increase in sensitivity to the following limits: Sb $\sim 10^{-4}$%, Bi $\sim 5 \cdot 10^{-6}$%, Cd $\sim 10^{-4}$%, Pb $\sim 10^{-4}$%, Su $\sim 10^{-4}$%, Cu $\sim 10^{-5}$%. The mean square error of a single determination of these elements was ± 18-20%. The respective calibration curves are shown in Fig. 6. Evaporation temperature was 1600°. Sample weight — 50 mg. Evaporation time — 1.5 minutes. In order to achieve these sensitivity limits, the spectra of two electrodes + impurities were photographed one after the other on the same place on a photographic plate; in the case of antimony determinations — the spectra of 4 electrodes + impurities were photographed. This is a consequence of the fact that increasing the weight of test sample four times is not equivalent to multiplying the sensitivity by four, since, in certain cases, the extent of evaporation of impurities decreases with increasing sample weight, for a given diameter and depth of the carbon beaker. Moreover, in the case of evaporation from a comparatively large sample, the film of condensate on the capsule is thick and unstable, and breaks down without excitation on the first impact of the spark. Evaporation in a vacuum gives a more stable film.

TABLE 4

Extent of Evaporation of Impurities During Vacuum Evaporation from Al_2O_3 (in %). (Measurements were made with relative errors of not more than ± 6%).

Temperature / Isotope	1000°	1200°	1400°	1600°*	1800°	2000°
Cd^{115}	76	90	98	98	97	93**
Sb^{122}	71	75	91	95	96	90**
Bi^{208}	78	89	94	98	96	94**
Pb^{210}	70	84	94	96	96	95
Sn^{123}	38	74	80	90	93	94
Cu^{64}	12	41	78	85	87	85

---

* At temperatures greater than 1700°, evaporation of Al_2O_3 starts.

** A decrease in condensation of Cd, Sb, and Bi at high temperatures is connected, apparently, with evaporation in reverse of the impurities from the upper capsule, because of strong heating of the latter. The extent of condensation in this case, depends on the intensity of cooling of the capsule.

The source in which spectrum excitation of impurities removed from the principal element by evaporation was carried out was an IG-2 spark generator working under the following conditions: C = 0.01 µF, L = 0.15 mH, I = 2A. Spectrograms were obtained by means of an ISP-22 spectrograph with a one-lens system of slit illumination; spectrograms were recorded on "Spectrographic Type III" plates.

Analysis was carried out on the basis of the following lines (spectrogram background was used as a reference line): Cd — 2288.02 A; Sb — 2598.06 A; Bi — 3067.7 A; Pb — 2833.07 A; Sn — 2839.9 A; Cu — 3247.5 A.

Determination of the extent (completeness) of evaporation of impurities from aluminum oxide, determination of the extent of their condensation on carbon capsules, and determination of optimum evaporation conditions were carried out by means of the radioactive isotopes of the elements composing the impurities.

Table 4 contains values for the extent of condensation of Cd, Sb, Bi, Pb, Sn, Cu on evaporation from Al_2O_3 at various temperatures. Evaporation time was 1.5 minutes. Increasing the time further did not appreciably increase the percent extraction of impurities from Al_2O_3. Sample weight was 50 mg.

Examination of Table 4 shows that the optimum conditions for evaporation are: temperature range 1200-1600° for Cd, Sb, Bi, Pb, Sn; 1400-1600° for Cu.

Our experiments with radioactive indicators showed that during the analysis of pure aluminum oxide* for cadmium by photographing the spectra for five capsules + impurities, on the same place on a photographic plate, it is possible to get a sensitivity of 10^{-6}%, thanks to the volatility and practically 100% evaporation of cadmium. Fig. 7 illustrates the calibration curve for cadmium, meaned from six measurements. In the same way, by photographing the spectra for 6 capsules + impurities on the same place on a plate, we succeeded in getting a limiting sensitivity for the determination of zinc in aluminum oxide of 10^{-6}%. The mean square error of a single determination of cadmium was ± 21%, and for zinc ± 18%.

The vacuum evaporation method was developed by A. N. Zaidel, N. I. Kaliteevsky, L. V. Lipis, and M. P. Chaika. Application of the method to the analysis of Al_2O_3 was carried out by Yu. I. Belyaev.

The authors wish to thank Academician A. P. Vinogradov and Corresponding Member of the USSR Academy of Sciences, S. E. Frish, for the interest they showed in this work.

SUMMARY

A new spectrographic method of analysis has been developed; it is called the vacuum evaporation method. By means of this method it is relatively easy to determine small concentrations of volatile impurities in a slightly volatile base material, with a sensitivity which is appreciably higher than that of known methods of spectrographic analysis. The vacuum evaporation method is based on preliminary evaporation of impurities from test material and their condensation on the surface of a cooled or graphite electrode; this electrode is then further subjected to spectrographic analysis. The mean square error of a single determination of impurities by the method suggested is 10-20%. It depends on the element to be determined, its concentration, and the nature of the base material from which it is to be separated.

The evaporation method has been used for the determination of Cd, Sb, Bi, Cu, Sn, and Pb in aluminum oxide.

Received August 12, 1955.

LITERATURE CITED

[1] A. K. Rusanov, "Spectrographic Analysis of Ores and Minerals". State Geol. Press, 1948.

[2] B. Scribner and H. Mullin, J. Research Nat. Bur. Standards, 37, 379 (1946).

[3] A. Rouse, J. Optical Soc. Am., 40, 82 (1950).

[4] I. I. Levintov, Bull. Acad. Sci. USSR, Phys. Series, 9, 699 (1945).

[5] S. L. Mandelshtam, N. N. Semenov, and Z. M. Turovtseva, J. Anal. Chem., 11, 9 (1956) (T. p. 7)**.

---

* Purest aluminum oxide was obtained by prolonged calcining, with periodic mixing, in a vacuum evaporator at 1700°.

** T. p. = C. B. Translation pagination.

MAINTENANCE OF TEMPERATURE CONDITIONS DURING PHOTO-COLORIMETRIC DETERMINATION OF SODIUM BY MEANS OF $NaNi(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$

A. I. Krupkin and G. A. Lorina

Little attention has been given in the literature to the question of maintenance of temperature conditions during precipitation of sodium ternary uranyl acetates. Remarks made by Kolthoff and Barber [1], Caley and Baker [2], and Hopkins and Williams [3], about the necessity of maintaining a definite temperature during precipitation of the salts do not say anything about the quantitative side of the question. More detailed information is given by Kogler [4], and also by Mecance and Shipp [5]; nevertheless, what they have to say is not enough, and the recommendations of the latter that the temperature should be kept at 0° introduces considerable inconveniences into the analysis. Meanwhile, since the determination of sodium colorimetrically by means of the ternary salt [6] is being introduced into a number of laboratories, considerable difficulties, connected with temperature variation, have cropped up.

In order to straighten out the question of temperature control, we carried out special tests. Sodium was precipitated as $NaNi(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$ which was then subsequently determined by means of nickel dimethylglyoxime, according to a method published previously [7].

The work was carried out bearing in mind laboratory conditions where air temperature may vary within the limits 20 ± 10°.

Preliminary calibration of the photoelectric colorimeter was carried out by means of a standard solution of nickel carbonate, followed by subsequent conversion of the salt into the dimethylglyoxime compound in individual lots containing the necessary amounts of nickel.

During sodium determination, the temperature may show its influence: 1) during precipitation of the ternary salt, 2) during filtration of salt from the solution and, finally 3) during the actual colorimetric part of the analysis.

The last stage has already been checked [7]. Within the temperature range indicated above, temperature has no essential effect on the accuracy of analysis during this stage.

During removal of the salt from mother liquor, it is only in contact with wash liquor for a short time during filtration under a reduced pressure of 500-600 mm Hg. As shown experimentally, changes of temperature have no effect on the accuracy of determination at this stage of the analysis.

It is therefore the stage during which the ternary salt is formed that must be studied in detail. Experiments were carried out in the following order: the temperature of all solutions (test material, precipitant, and alcohol) when they were poured together was kept at 20 ± 1°, while the temperature of the thermostat in which test samples were kept for 16-20 hours, could be adjusted to operate at 10, 20, 30, 40, and 50 ± 1°.

Experimental results are plotted in Fig. 1.

Displacement of the graph obtained during analysis, when the thermostat was kept at 30°, with respect to the graph obtained for nickel carbonate solutions, is explained by an increase in results in the first case as a consequence of nickel being held back from the precipitant solution by the filter disc. When this nickel gets into the solution of the sodium salt during the colorimetric part of the analysis, it leads to systematic errors; when these systematic errors were eliminated, the graphs obtained during calibration by both methods coincided. This indicates that on thermostating test samples at 30°, and leaving them for 16-20 hours, complete precipitation of sodium salts occurs. Lowering the temperature leads to precipitation of the ternary salt from the precipitant, which makes the results too high. This increase in the results is more appreciable in the range 20-30°, than in the range 10-20°. For a temperature of 10°, the shift of the graph with respect to that obtained at 20°, is so insignificant, that the results obtained at temperatures of 10-20°, can be related to the results of the last temperature (20°) without introducing appreciable errors into the analysis. At temperatures greater than 30-35°, the amount of precipitated salt decreases appreciably. When the amount of sodium salt precipitated at 30° is taken as 100%, the amount precipitated at other temperatures have the values given in Table 1.

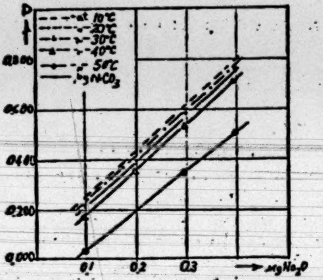


Fig. 1. Shift in calibration curves obtained on the FEK-M apparatus with changes in temperature during precipitation of $NaNi(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$.

TABLE 1

Precipitation of the Sodium Salt at Various Temperatures

Sodium oxide introduced in mg	Sodium oxide determined at various temperatures (°C), as % of the amount introduced				
	50	40	30	20	10
0.1	8	81	100	118	120
0.2	45	86	100	107	108
0.3	58	91	100	104	105
0.4	65	92	100	102	102

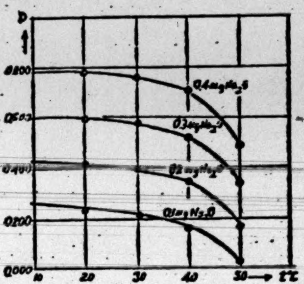


Fig. 2. Changes in the amount of $NaNi(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$ during precipitation at various temperatures.

TABLE 2

Increase in Experimental Errors During Sodium Determination, with Increasing Temperature During Precipitation

Sodium oxide introduced in mg	Relative experimental error in %, during salt precipitation at temperatures given below in °C				
	10	20	30	40	50
0.1	5.0	2.5	3.5	13.0	14.0
0.2	2.5	1.8	2.5	4.5	9.5
0.3	1.0	1.0	1.3	4.0	5.0

The relation between amount of salt precipitated and temperature is shown in Fig. 2.

In the temperature range 10-20°, the graph is approximately linear in character for all the sodium concentrations tested. Accordingly, as we have noted above, results obtained at temperatures below 20° can be related to this temperature.

In the range 20-30°, the amount of precipitated salt falls more rapidly. In general, the shape of the curve can be expressed by the following formula:

$$D_{30}^{\circ} = D_{T}^{\circ} - K(30 - T^{\circ}),$$

where D_{30}° – is the optical density of solutions obtained on precipitating the salt at 30°.

D_{T}° – the optical density of solutions obtained on precipitating the salt at a given temperature T°. In the range 20-30°; $K = \Delta D / \Delta T^{\circ}$ is a correction coefficient.

For temperatures in the range 20-30° this correction coefficient proved to be 0.025 for the apparatus we used.

On increasing the temperature further, apart from a rapid drop in the amount of salt precipitate, the reproducibility of analysis also deteriorates, as is evident from the results given in Table 2. The results obtained show that at temperatures greater than 30° analysis with the required accuracy is impossible.

Taking into account the fact that precipitation of sodium takes 16-20 hours, and that it is hardly possible to keep the temperature of the laboratory itself constant within ± 1° during this time, it is recommended that a thermostat should always be used, and that the salt should be precipitated at 30°. If this is done, then there is no need for additional calibrations and calculations.

If the temperature of the laboratory can be kept within the limits of 10-20°, analysis could be carried out without a thermostat. In such cases however, it would be necessary to calibrate the apparatus for 20° as well, which is scarcely justifiable.

Changes in laboratory temperature may lead to changes in the amount of ternary salt added to the precipitant to saturate it. To avoid errors which spring from this cause, it is essential to keep the precipitant for 1-2 hours before use in contact with the ternary salt at 20°, and only filter it free from the salt after this time has elapsed.

Solutions of test material, precipitant, and alcohol should all be kept at 20° before they are added together.

SUMMARY

1. Formation of the salt $NaNi(UO_2)_3X(CH_3COO)_9 \cdot 6H_2O$ in the temperature range 10-50° has been evaluated quantitatively.

2. The amount of precipitated salt changes appreciably in the temperature range indicated.

3. Analysis can be carried out at 20 ± 10°, with thermostating of the solution at 30 ± 1°.

Received October 31, 1955

LITERATURE CITED

[1] J. M. Kolthoff, B. B. Barber, J. Am. Chem. Soc., 50, 1625 (1928).

[2] R. Caley, W. Baker, Ind. Eng. Chem., 11, 604 (1939).

[3] Hopkin and Williams, Organic Reagent for Metals, London, 1946, p. 158.

[4] F. Kögler, Angew. Chem., 48, 561 (1935).

[5] R. Mecance, H. Shipp, Biochem. J., 25, 2, 449 (1931).

[6] A. I. Krupkin, Factory Labs., 16, 1, 31 (1950).

[7] A. I. Krupkin, Factory Labs., 18, 7, 786 (1952).

BLANK
PAGE

THE SPECIFIC CHARACTER OF THE ELECTRONIC ABSORPTION SPECTRA OF MOLECULES (THE CHROMOPHORE THEORY).

F. Sh. Shifrin

The A. I. Herzen Leningrad State Pedagogic Institute

Absorption of light by organic compounds in the visible and near ultra-violet, which determines, with certain reservations, their color, is connected with the presence of special atomic groups or chromophores in these compounds. The color of a chromophore is not made up of the colors of its separate parts; a chromophore is "indivisible". A chromophore possesses a known independence of the rest of the molecule; it is "autonomous", and, what is essential from the point of view of structural analysis, its light absorption exhibits a specific character, or, more simply, the chromophore possesses a specific character; i.e. when a chromophore is present in various compounds in which the surrounding atoms or groups, or its immediate neighborhood, differ, it gives rise to (under standard conditions — aggregate state, solvent, thickness of absorption film, etc. — which are the same for all the compounds) the same light absorption.

The experimental facts enumerated can be physically interpreted as follows.

A chromophore contains a system of weakly-bound electrons, π-electrons, the transfer of which from a normal to the nearest excited level corresponds approximately to the visible part of the spectrum. These electrons are collectivized (held in common) within the confines of the chromophore (π bond conjugation); from this fact springs the "indivisibility" of the chromophore*; the region in which they can move about, their "cloud", is covered to a comparatively small extent by the "clouds" of other electrons in the molecule; from this fact springs the "autonomous" property of the molecule, its specific character.

Light absorption is characterized below, by the wave length λ, corresponding to the maximum, or long-wave "red" edge of the longest-wave absorption band (region)**. The values of λ which are always given in Angstroms, and which, unless it is stated otherwise, refer to values obtained for the vapor phase of a compound — at the red edge — are taken from published results [2]. Apart from results which refer to vapors, where the structure and light absorption of a molecule is least distorted by inter-molecular interaction, we have also used results obtained for solutions, preferably, in indifferent solvents; the latter results also have their advantages.

Concretization of chromophores is suggested in the present article.

1. Analysis of experimental results shows that the specific character of certain chromophores is not very marked. E. g. for molecules containing the chromophore $> C = C <$, i.e. one isolated ethylene bond, λ has values ranging from 1745 for ethylene, to 2320 for tetramethylethylene.

We shall show that it is possible, by concretizing the chromophores, to increase the specificity of the specific character, and that this opens up additional possibilities for structural analysis.

Actually, the different light absorption exhibited by the same chromophore in different molecules is determined by differences in the surroundings of the chromophore (i.e. differences in neighbouring atoms or groups). A chromophoric group is only "autonomous", and is not completely independent of the rest of the molecules. The light absorption of a chromophore can only be regarded in a certain sense, or as a "null" approximation, as independent. In the following approximate treatment, it will be necessary to take into account

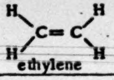
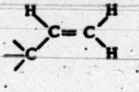
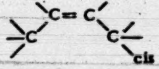
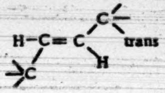
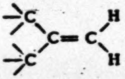
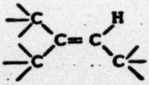
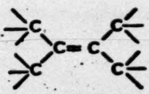
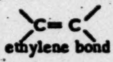
---

* Division of a chromophore, in particular, the ethylene group $-CH = CH-$ into two chromophores (the individual carbon atoms are taken as such) [7], is pointless.

** It is of interest to carry out a further analysis of results, by considering, in addition, intensity, band structure, absorption curves as a whole, etc. but we are confining ourselves here to wave length λ.

TABLE 1

Light Absorption of Hydrocarbons Containing Isolated Ethylene Bonds

Experiment number	Immediate neighbours of the ethylene bond	Concretized chromophore	Limits of λ	Table on which information given in Table 1 is based
1	4 hydrogens	 ethylene	~1745	
2	3 hydrogens 1 carbon		1850-1900	2
3	2 hydrogens 2 carbons	symmetrical disubstituted	2010-2110	
3a			2040-2110	3
3b			2040*	
		unsymmetrical disubstituted		
3c			2010-2040	4
4	1 hydrogen 3 carbons		2160-2200	5
5	4 carbons		2320**	
	Generalized	 ethylene bond	1745-2320	

* Transdimethylethylene

** Tetramethylethylene

TABLE 2

Light Absorption of Alkyl-ethylene

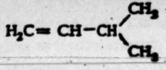
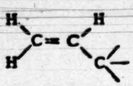
Experiment number	Compound	λ
1	$H_2C=CH-CH_3$	1850
2	$H_2C=CH-C_2H_5$	1875
3	$H_2C=CH-C_3H_7$	1884
4	$H_2C=CH-C_5H_{11}$	1886
5		1895
Generalized		1850-1900

TABLE 4

Light Absorption of Unsymmetrical Dialkyl-ethylenes

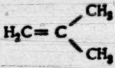
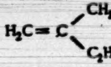
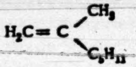
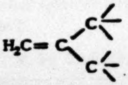
Experiment number	Compound	λ
1		2020
2		2010
3		2040
Generalized		2010-2040

TABLE 3

Light Absorption of Symmetrical Cis-Dialkyl-ethylenes

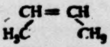
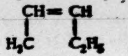
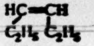
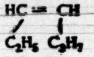
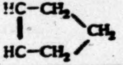
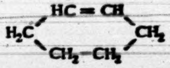
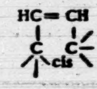
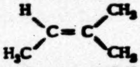
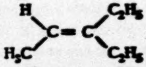
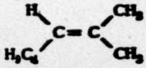
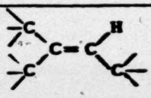
Experiment number	Compound	λ
1		2080
2		2060
3		2040
4		2040
5		2100
6		2110
Generalized		2040-2110

TABLE 5

Light Absorption of Tri-alkyl-ethylenes

Experiment number	Compound	λ
1		2200
2		2160
3		2160
Generalized		2160-2200

the interaction of the chromophoric group with the rest of the molecule. The question is, what can be used as an approximation. To answer this question, let us turn to the theory of molecular structure, to Butlerov's theory as developed by Markovnikov.

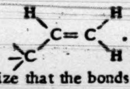
"It may be assumed", wrote Markovnikov, "that in general, the influence of any element on another is weakened in proportion to their distance apart in the common chain of chemical action, holding all the elements in a particle" [1].

Guided by this idea, one must therefore, first of all take into account the interaction of its immediate neighbors, including the atoms of the chromophore itself, with the chromophore (this means taking into account $\sigma-\pi$ conjugation, and maybe, even $\sigma-\sigma$ conjugation). To a given chromophore therefore, there will correspond several concretized chromophores, each of which contains the given chromophore, with different immediate "neighbors" (classification of compounds according to their chromophores results in more "branching"). It is understandable that concretized chromophores should possess a more developed specific character than ordinary chromophores. In order that the increase in the specificity of the specific character should be appreciable, it is necessary that these mutual effects, which are essential here, do not simply decrease with increasing distance apart of the atoms from each other, but should decrease fairly rapidly. This, apparently, is what does occur. Let us trace the part played by concretization, taking as examples the simplest, but at the same time important chromophores: the ethylene bond, the carbonyl group etc.

To start with, we shall confine ourselves to compounds containing just one chromophore, or several similar but disconnected chromophores. Standardization is particularly essential here, because deviations from it may reflect on λ to a greater extent, than differences between concretized chromophores.

2. Ethylene and carbonyl chromophores. The limiting values of λ for concretized chromophores are given in the tables. Table 1 contains data on chromophores containing isolated ethylene bonds (we have confined ourselves to hydrocarbons), while Table 6 contains data on chromophores containing carbonyl groups. These limits were obtained from a survey of a comparatively small, but different, number of experimental results (results on which Table 1 is based are given in Tables 2-5, while the results on which Table 6 is based are given in Tables 7-9) which, while only serving as orientating results, nevertheless, indicate the significant gain in specific character obtained by concretizing chromophores.

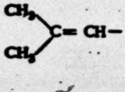
We shall clarify what we have in mind by reference to the tables.

The formula , signifies that three other atoms or radicals can be linked via simple bonds (in order to emphasize that the bonds are simple ones, we have depicted the three valency links by an open fan) to the carbon atom with free valencies.

The nearness of the values of λ to each other in columns 3a, 3b and 3c of Table 1 shows that here, the way the neighboring atoms are arranged around the ethylene bond is not so important, as what the neighboring atoms are (2 hydrogens, 2 carbons).

In noting the significant shift in λ for cyclopentene or cyclohexene, as compared with ethylene (~2100 instead of 1745), the batochromic effect of ring closure is sometimes referred to. Nevertheless, from the point of view of concretized chromophores, to speak, in connection with the given samples of the special effect of ring closure is superfluous — λ of these cyclic compounds should be compared, not with λ of ethylene, but with λ of butene-2 or other compounds (Table 3) containing the same concretized chromophore. The light absorption values of symmetrical cis-dialkyl-ethylenes and of some compounds with an isolated ethylene bond are given in Table 3.

V. M. Chulanovsky, in this connection, correctly compares the light absorption of n_1-butene and n_1-heptene with the light absorption of 2-methyl-2-butene and that of 3-hexene; he makes the valuable observation that, "in essence, one should, in all these cases talk notof one and the same chromophoric group of ethylene $>C=C<$, but of three different chromophoric groups

$H_2C=CH-$, $-CH=CH-$ or 

$$(CH_3)_2C=CH-$$

in the last two cases" [6].

Results (taken from [3]) for other standard conditions — for maxima in solution — are compared among themselves for carbonyl compounds, as well as results relating to the red edge in the vapor state. Because of insufficient experimental data, not all the columns in Tables 6-8 have been filled.

3. In the series of Molecules I-IV the chromophore ($-S-C\equiv N$ or others) have the same immediate neighbors, i.e. it is "concretized".

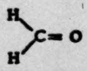
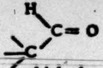
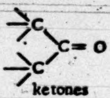
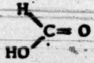
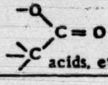
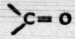
I. Thiocyanates: $CH_3-S-C\equiv N$... 2630; $C_2H_5-S-C\equiv N$... 2620;

II. Amines [2, 5]: CH_3NH_2... 2400; $C_2H_5NH_2$... 2400; CD_3NH_2... 2400; CH_3ND_2... 2360; CD_3ND_2... 2385;

III. Alcohols: methyl — 1607, ethyl — 1633; the following results refer to the center of the diffuse absorption band: ethyl — 1518, propyl — 1565, butyl — 1577.

TABLE 6

Light Absorption of Compounds Containing Isolated Carbonyl Groups

Experiment number	Immediate neighbors of the carbonyl group	Concretized chromophore	Limits of λ		Table on which information given in Table 6 is based
			Red edge in the vapor	Maximum in solution	
1	2 hydrogens	 formaldehyde	3750*		
2	1 hydrogen 1 carbon	 aldehydes	3361-3485	2775-2825	7
3	2 carbons	 ketones	3200-3330	2703-2858	8
4	1 hydrogen 1 oxygen	 formic acid		2060**	
5	1 carbon 1 oxygen	 acids, etc.		2040-2170	9
	Generalized	 carbonyl	3200-3750 (acids not taken into account)	2040-2858 (formaldehyde not taken into account)	

---

* λ values from [4].

** In water [8].

TABLE 7

Light Absorption of Saturated Aldehydes

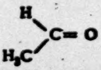
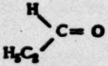
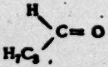
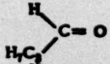
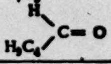
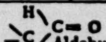
Experiment number	Compound	λ in vapor, red edge	Literature reference	λ in solution, maximum
1		3485	[4, 5]	2775
2		3400	[4, 5]	2788
3	 N.	3400	[2]	2825
4	 iso-	3400	[2]	
5	 iso-	3361	[5]	
Generalized	 Aldehydes	3361-3485		2775-2825

TABLE 8

Light Absorption of Saturated Ketones

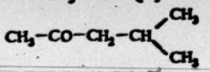
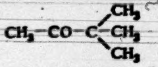
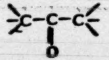
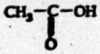
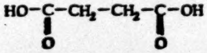
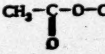
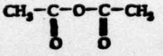
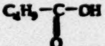
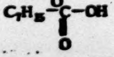
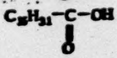
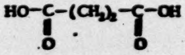
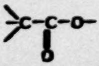
Experiment number	Compound	λ in vapor, red edge	λ in solution, maximum
1	$CH_3-CO-CH_3$	3330	2706
2	$CH_3-CO-CH_2\cdot CH_2\cdot CO-CH_3$		2708
3	$CH_3-CO-C_2H_5$	3200	2703
4	$CH_3-CO-C_4H_9$	3200	2795
5	 $CH_3-CO-CH_2-CH{<}\substack{CH_3\\CH_3}$		2813
6	 $CH_3-CO-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$		2858
7	$CH_3-CO-(CH_2)_5-CH_3$		2778
8	$C_2H_5-CO-C_2H_5$		2748
9	$C_2H_5-CO-C_3H_7$		2858
10	$C_3H_7-CO-C_3H_7$		2810
Generalized	 $>C-\underset{\underset{O}{\|}}{C}-C<$	3200-3330	2703-2858

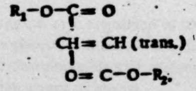
TABLE 9

Light Absorption of Saturated Acids, Esters and Anhydrides([8], unless indicated otherwise).
Solvent: A—alcohol; W—water; H—heptene.

Experiment number	Compound	λ, maximum, solvent
1	 $CH_3-\underset{\underset{O}{\|}}{C}-OH$	2040 H 2080 W [3]
2	 $HO-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OH$	2080 [3]
3	 $CH_3-\underset{\underset{O}{\|}}{C}-O-C_2H_5$	2100 A
4	 $CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3$	2170
5	 $C_4H_9-\underset{\underset{O}{\|}}{C}-OH$	2040 H 2060 W
6	 $C_7H_{15}-\underset{\underset{O}{\|}}{C}-OH$	2040 H
7	 $C_{15}H_{31}-\underset{\underset{O}{\|}}{C}-OH$	2100 W
8	 $HO-\underset{\underset{O}{\|}}{C}-(CH_2)_2-\underset{\underset{O}{\|}}{C}-OH$	2070 W
Generalized	 $>C-\underset{\underset{O}{\|}}{C}-O-$	2040-2170

The amino and hydroxyl groups are usually referred to as auxochromes, not chromophores; we do not see much point in distinguishing between the two; since these groups are saturated, taking into account immediate neighbors means taking into account σ-conjugation.

IV. In a series of compounds of the type



fumaric acid and its derivatives* the values of λ (maximum in solution [8]) for different pairs R_1 and R_2 connected to the same concretized chromophore, are similar to each other: $R_1 = H$, $R_2 = H$, $\lambda = 2070$ in alcohol and 2100 in hexane; $R_1 = H$, $R_2 = Na$, $\lambda = 2070$ in water; $R_1 = Na$, $R_2 = Na$, $\lambda = 2040$ in water; $R_1 = CH_3$, $R_2 = CH_3$, $\lambda = 2080$ in hexane.

4. Some exceptions: 1) In some cases the specific character loses its specificity to some extent, e.g. for isothiocyanates: CH_3NCS... 3010, C_2H_5NCS... 2860. This may be a consequence of incomplete standardization of experimental conditions (including the method of spectra recording) for measuring the light absorption. In our case we may mention that λ for CH_3NCS is referred to a higher pressure (19 mm) than for C_2H_5NCS (11 mm); naturally, with increasing pressure, the region where absorption is registered extends further.

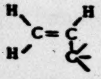
The idea of standardization of conditions is not completely satisfactory; refined analysis is necessary. In this connection perhaps, it would be preferable to take λ for maxima and not for the red edge — where this is possible.

2) Let us consider e.g. the concretized chromophore $>C-\overset{O-}{C}=O$ (No. 5 in Table 6). In general, it cannot be assumed that the nature of the atom or radical connected to carbon by three vacant single bonds (this was suggested above in connection with color), has only a little effect on the properties of the carboxyl group; it is known that for CH_3COOH the dissociation constant $K = 1.82 \cdot 10^{-5}$, while for $ClCH_2COOH$ $K = 155 \cdot 10^{-5}$. The change in the constant is explained by the inductive effect**. The inductive effect, apparently, is much less marked when it is a question of color. All the same, when one is dealing with strongly polar groups (e. g. CO) one must be careful.

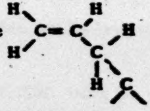
3) In molecules (I) $H_2C=CH-CH_3$ and (II) $H_2C=CH-CH_2-CH=CH_2$ the concretized chromophore is the same ($H_2C=CH-C\langle$) and we can expect similar values of λ for them. This is true when CH_2 prevents conjugation, and isolates the double bonds from each other [otherwise, λ for (II) would differ appreciably from λ for (I)]. In the presence of strong polar groups this may be doubtful too.

5. In proposing concretization of chromophores, we take into account the immediate neighbors of the chromophore, or in other words the first zone of neighbors (usually, $\sigma - \pi$ conjugation). Further concretization is possible by taking into account the second zone — i.e. atoms directly linked to atoms in the first zone ($\sigma - \sigma$ conjugation), a third zone etc. It would be natural to expect that when this is done, the specificity will increase all the time, and the limits of λ will become narrower. This can be illustrated by means of results for ethylene chromophores (Tables 1 and 2).

For the chromophore $>C=C<$ the limits of λ are 1745-2320, for the concretized chromophore



the limits narrow to 1850-1900, and for the doubly concretized chromophore



(molecules 2, 3, 4, Table 2) the limits are narrower still. 1875-1886.

---

* The chromophore is fairly complicated in this instance: it includes an ethylene group and two carbonyls.

** Markovnikov's words quoted above, re the weakening of interaction between atoms, with increasing separation from each other in true here also: for $ClCH_2CH_2COOH$ $K = 8.5 \cdot 10^{-5}$; for $Cl(CH_2)_3COOH$ $K = 3 \cdot 10^{-5}$; for $Cl(CH_2)_4COOH$ $K = 2 \cdot 10^{-5}$.

In large complex compounds, structural analysis of which is most complicated, the chromophores may be repeated in various compounds together with one or several zones of neighboring atoms, in one and the same nearest environment.

Identification is usually accepted as recognition of molecules as a whole, or of chromophores. The introduction of concretized chromophores eliminates this distinction; it is also possible to identify intermediate (between normal non-concretized chromophores and molecules as a whole) assemblies of atoms — chromophores with varying numbers of neighboring zones of atoms.

6. Concretization of chromophores and the analysis of experimental results connected with it, are of interest from various theoretical and practical points of view: in the first instance, for checking and bringing together the ideas of Butlerov and Markovnikov on the basis of new material. When Butlerov in 1861 propounded his theory of chemical structure, he did not have at his disposal information on color and spectrographic data which are available nowadays. All this came afterwards. Secondly, for developing the chromophore theory itself, for analyzing the accuracy of theoretical calculations which are normally confined to consideration of systems of the π-electrons of molecules, and for studying super-conjugation.

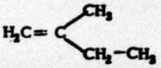
It is also possible, that a similar concretization (of the first, second, and other neighboring zones) would be a useful method for studying not only electronic spectra, but other physical and chemical properties of molecules and crystals.

Thirdly, for structural analysis. Once it has been settled how the nearest neighboring zones of the chromophore affect its light absorption, it should be possible to do the reverse: to decide from the light absorption, not only what the chromophore is, but what its immediate neighboring zones are.

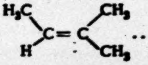
Let us consider the following examples: 1) Let us assume that in the case of a hydrocarbon C_5H_{10}, the position of the edge of long-wave absorption in the vapor (under certain conditions) has been found to be at λ = 1884. This lies within the range 1745-2320 for one ethylene bond. Without concretization of the chromophores, we cannot however, decide between the following isomers:

I) $H_2C{=}CH{-}CH_2{-}CH_2{-}CH_3$ ... pentene 1

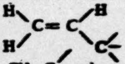
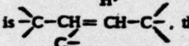
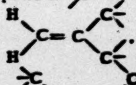
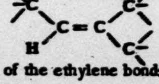
II) $H_3C{-}CH{=}CH{-}CH_2{-}CH_3$ ... pentene 2

III)  unsymmetrical methylethyl-ethylene

$H_2C{=}C(CH_3)(CH_2{-}CH_3)$

IV)  ... trimethyl-ethylene

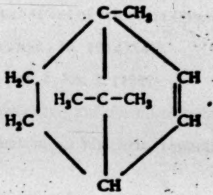
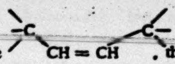
$(H_3C)(H)C{=}C(CH_3)(CH_3)$

Having concretized the chromophores, the appropriate formula is found to be (I), because λ = 1884 falls within limits .. ~1850-1900 for the concretized chromophore , present in formula (I); for formula (II), where the concretized chromophore is , the range is ~2040-2110; for formula (III) where the concretized chromophore is , the range is ~2010-2040, and for formula (IV) where the concretized chromophore is  the range is ~2160-2200. Using this value of λ we can decide what are the neighbors of the ethylene bond: 3 hydrogens, and 1 carbon; only formula (I) out of the four isomers (I—IV) has these neighbors. This example as well as those that follow, show how concretization of chromophores can help to establish the position of a double bond, and to make a choice between several isomers[*]

---

[*] In addition, narrowing of the limits, which occurs when a chromophore is concretized, makes the fact that λ for the molecule falls within the given range more convincing.

A problem of this type is met during the study of rubber e.g. It is known that the latter contains isolated ethylene bonds*.

2) Bornylene $C_{10}H_{16}$. If bornylene has the structure  , i. e. it contains the concretized chromophore  , then λ should fall within the range ~2040-2110. Experiment gives 2040 [10]. Incidentally, it is obvious, despite [10], that it is superfluous to speak of the special batochromic effect of ring closure in this case (compare above). There are various ethylene chromophores in other terpenes also.

3) λ for a compound C_4H_8O is found to be 3200 (or ~2703 for maximum in solution); for this compound there are two possible isomeric formulas: (I) a ketone $CH_3-CO-C_2H_5$ and (II) an aldehyde C_3H_7COH; we choose (I), since 3200 (~2703 for its solution), falls within the measured limits for ketones 3200-3330 (2703-2858) and not within the limits for aldehydes 3361-3485 (2775-2825).

Using the concept of concretized chromophores, it is possible to explain some interesting facts and regularities. An example follows.

Compounds of chemically different types such as acids, esters, and anhydrides in Table 9, possess similar values of λ** (the λ range is 2040-2170); on the other hand, for compounds of the same class — the alkenes Table 1 — λ differs appreciably from one to the other (the λ range is 1745-2320). This is easily explained if one remembers that the compounds in Table 9 all contain the same concretized chromophore, while those in Table 1 have different chromophores.

Moreover, this example (and others) show that differences in absorption spectra are not in line with chemical differences, i.e. compounds may still have similar spectra though there are considerable chemical differences between the compounds; and, vice versa, the spectra of chemically similar compounds may differ appreciably from each other. This means that electronic absorption spectra are not always specific enough as a means of identification. When dealing with analysis of compounds of various types where it is necessary to get reliable results, the various methods should be combined.

We hope that the ideas set forth in the present article may be of some assistance in developing methods for structural analysis of compounds containing chromophores. Such compounds include such industrially important ones as rubber, vitamins, and dyes, etc.

The author is indebted to Prof. V. M. Chulanovsky for discussing the present article in manuscript form.

SUMMARY

The concept of concretization of chromophores is advanced. Concretization of chromophores leads to an increase in the specific character of their light absorption, which is confirmed by analysis of experimental results; this concept widens the scope of structural analysis of compounds by means of their electronic absorption spectra and may be of theoretical interest.

Received August 2, 1954

---

* The absorption of polybutadiene, within the limits of experimental errors, coincides with that of dialkyl ethylenes such as octene-3 [9].

** V. Anri [3, p. 82], notes "The absorption spectra of the ester $C_nH_{2n+1}CO \cdot O \cdot C_pH_{2p+1}$ differs very little from those of the corresponding acid $C_nH_{2n+1}CO \cdot OH$".

LITERATURE CITED

[1] V. Markovnikov, "Material on the Mutual Effect of Atoms in Chemical Compounds", Kazan, 1869.

[2] H. Sponer, and E. Teller, Revs. Modern Phys., 13, 124 (1941).

[3] V. Anri, Trans. State Optical Institute, Vol. 1, No. 2, (1921).

[4] H. Sponer, Molekülspektren und ihre Anwendung auf chemisch Probleme I. Tabellen, Berlin, 1935.

[5] A. Saur, Electronenbandenspektren mehratomiger Molekeln, Landolt-Barnstein Tabellen, 6, [illegible]. 1951, p. 53.

[6] V. M. Chulanovsky, "Introduction to Molecular Spectral Analysis", Tech. Theory Press, 1950; Bull. Leningrad State University, 1950, 5 (No. 3); Prog. Phys. Sci., 43, 30 (1951).

[7] R. Vitsinger, "Organic Dyes", 1936, p. 15.

[8] J. R. Platt, H. B. Klevens, Revs. Modern Phys., 16, 182 (1944).

[9] H. B. Klevens, J. Polymer Sci., 10, 97 (1953).

[10] H. Ley, Handbuch d. Physik., 21 (1929).

SORPTION OF CERTAIN SURFACE ACTIVE DYES BY SULFIDES DURING AGING

N. A. Rudnev and L. I. Guseva

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, Moscow

INTRODUCTION

The surface of the precipitates formed, is of great importance for the phenomenon of coprecipitation of metals of the third group with sulfides of the hydrogen sulfide group. HS^- and S^{2-} ions* [1], are adsorbed on the strongly developed surface of sols of the compounds indicated, and of the gels formed by their coagulation; this may lead to coprecipitation of cations giving insoluble sulfides. It is from this viewpoint that Kolthoff and his coworkers explained coprecipitation of zinc with the sulfides of copper (II), mercury (II), and bismuth [2-4], which they studied.

In our studies [5, 6], it was established that there is a clearly marked difference between coprecipitation of zinc with HgS, CdS, and SnS_2 on the one hand, and with Ag_2S, PbS, As_2S_3, and Sb_2S_3 on the other. Moreover, it was found that under conditions of rapid saturation of solution with hydrogen sulfide, when the surface of the precipitate which forms is particularly large, coprecipitation of zinc with the first group of sulfides indicated above increases rapidly, while coprecipitation in the case of sulfides of arsenic (III), antimony (III), lead, and bismuth is insignificant. It would have been natural to expect however, that coprecipitation of zinc, as a result of the reason advanced above, should be just about the same for the various sulfides. Otherwise, this would suggest large differences in the surface area of the sulfides, or in the amount of HS^- and S^{2-} ions adsorbed – a difficult assumption.

The question under discussion is accordingly very complex, and has other unclarified features. A detailed study of surface phenomena in sulfides should give a clearer solution of questions bearing on the nature of coprecipitation.

The interaction of sulfides with organic surface active materials is the subject of the work described here. Basic dyes which are strongly sorbed by negatively charged sols [7] were used for this purpose. In addition, since aging plays an important part in coprecipitation of cations with sulfides, the kinetics of sorption of dyes by the compounds indicated was also studied. By means of such a method it was intended to explain the changes in magnitude and structure of the surface of sulfide particles during their aging.

A large amount of work was devoted to the interaction of colloids, their mutual coagulation, and also to their sorption by various materials. As far as we know, no work along the lines indicated has been carried out before.

In our work, the effect of dyes on the sulfides was studied under normal analytical conditions.

Picton and Linder [8], as long ago as 1897, found that when dyes of opposite charge interact, precipitation ensues.

Biltz [9] established a rule according to which, colloids of opposite charge precipitate each other only when they are present in equivalent amounts in solution. When one colloid is in excess, no precipitation is observed.

An interesting study, devoted to interaction of dyes with various materials, was published by Rheinbold and Wedekind [10]. They found that basic materials couple up acid dyes particularly well, while on the other hand, acid materials couple up basic dyes.

---

* Linder and Picton point out that CuS is precipitated as the hydrosulfide with a formula corresponding to $7CuS \cdot H_2S$ and $9CuS \cdot H_2S$.

Later Koganovsky [11, 12]. studied sorption of substantive dyes, $Fe(OH)_3$, and $Al(OH)_3$ sols, and humic acids by gels of aluminum and ferric hydroxides respectively. The author has given a number of sorption isotherms and pointed out the anomalous, step-wise nature of the process.

Sheinker [13, 14]. studied the degree of dispersion of several dyes by a diffusion method, as well as their adsorption on glass: he found that if the dye dissolves unimolecularly in water, then the film formed on the glass surface is unimolecular. In this case, when the particles in solution are aggregated, the adsorption layer is unimicellular.

Again, Peneth [15]. and Khlopin and Merkulova [16]. also studied dye adsorption by crystalline precipitates, in order to determine their surface area.

In a series of papers, Kolthoff and coworkers [17, 18]. carried out similar research on determination of lead sulfate surfaces.

Slovnova [19]. studied the interaction of dyes of the thiazine series with the nitrates of barium, lead, and strontium during their crystallization; she found that methylene blue forms a solid solution with lead nitrate. In barium nitrate, the dye indicated grows preferentially as submicroscopic crystals, forming a micro-heterogeneous system.

So called "solid phase" color reactions, and adsorption indicators also belong to this group of studies dealing with interaction of organic materials with the solid phase.

Kuznetsov [20] has published a detailed review of solid phase reactions. Work carried out by Fajans [21]. and Rudenko [22]. has been devoted to the application of adsorption indicators in analytical chemistry.

We carried out experiments on sorption of dyes by sulfides, both during their formation (when the surface is small). and after separation of the solid phase.

Methyl violet and neutral red, in which the organic part is the cation, were used as surface active meterials.

Sulfide structure was studied by means of an electron microscope.

EXPERIMENTAL

Original Materials

0.1 M solutions of the chlorides of the hydrogen sulfide group of metals were used.

0.1 M Na_3AsO_3 was prepared for experiments with arsenic sulfide (III). Silver sulfide was precipitated from 0.1 M $AgNO_3$, while PbS was precipitated from 0.02 M $PbCl_2$. 0.5% solutions of the dyes were prepared prior to use.

Experimental Procedure

Into a 150 ml flask were introduced: a solution of the hydrogen sulfide group metal in such amount that the weight of precipitated sulfide would amount to 0.1 g, hydrochloric acid (1:1) to a concentration of 0.3 N, water, and 10 ml of a 0.5% solution of neutral red. The contents of the flask were diluted to a total volume of 100 ml. The flask was placed in a thermostat at 28°, and after 10 minutes, hydrogen sulfide was passed through at a rate of ~500 cm^3/minute for 5 minutes. The flask was not removed from the thermostat during passage of hydrogen sulfide. At the end of this time, 10 ml of water saturated with hydrogen sulfide was added to the contents; the stoppered flask was shaken for 20 minutes in a mechanical shaker. After the elapse of a certain time (See table below), 3-5 ml of solution was measured out, and the amount of dye remaining in it determined after centrifuging. Determinations were made colorimetrically with an accuracy of 3%. In cases where neutral red was added after precipitate formation, the procedure was similar, but with the difference that instead of 10 ml of water saturated with hydrogen sulfide, the same amount of the dye indicated, was added.

The first series of experiments were carried out to get an idea of the extent of the sorption of dyes by various sulfides at the moment of their formation, when they have a very developed surface.

From experiments with methyl violet it became evident that this dye is absorbed by a number of sulfides, but, as a result of action of hydrogen sulfide, there is a change in its color which precludes using a colorimetric finish. Further experiments were therefore carried out with neutral red, the color of which in 0.3 N HCl is not changed by H_2S, since the oxidation-reduction potentials of this dye and H_2S respectively, for the given acid concentration, have roughly equal values.

Experimental results are given in Table 1.

TABLE 1

Sorption of Neutral Red by Hydrogen Sulfide Group Metal Sulfides with Time*
Sorbent: 1000 mg/liter of MeS or Me_2S_3; c_0 = 500 mg/liter (dye added before passage of H_2S); pH 0.52; t 28°; volume of solution 110 ml.

Experiment number	Group	Metal sulfide	Initial concentration of dye (c_0) in mg/liter	Equilibrium concentration of dye (c) in mg/l after 1/4 hour	Amount of sorbed dye c_0-c/m after 1/4 hour		Equilibrium concentration of dye (c) in mg/l after 24 hours	Amount of sorbed dye c_0-c/m after 24 hours	
					in mg/g	in %		in mg/g	in %
1	I	HgS	500	268	232	46.6	195	305	61.2
2		Bi_2S_3	500	250	250	50.0	131	369	73.8
3		Sb_2S_3	500	199	301	60.4	118	382	76.4
4		SnS_2	500	256	244	48.8	106	394	78.8
5	II	CuS	500	83	417	83.4	154	346	69.3
6		Ag_2S	500	209	291	58.2	237	263	52.6
7	III	CdS	500	105	395	79.0	106	394	78.8
8		As_2S_3	500	14	486	97.2	17	483	97.7
9		PbS	500	276	224	44.9	251	249	45.9

---

* The results given in this table are the means values of 4-5 parallel tests.

TABLE 2

Sorption of Neutral Red by the Sulfides HgS, Sb_2S_3, CuS and As_2S_3 on Aging
Sorbent: 1000 mg/liter of MeS or Me_2S_3; c_0 = 500 mg/liter (dye added before passage of H_2S); pH 0.52; t 28°; volume of solution 110 ml.

Experiment number	Metal sulfide	Amount of dye sorbed c_0-c/m after									
		1/3 hour		24 hours		48 hours		72 hours		96 hours	
		in mg/g	in %	in mg/g	in %	in mg/g	in %	in mg/g	in %	in mg/g	in %
1	HgS	247	49.4	325	64.9	–	–	350	70.0	–	–
2	Sb_2S_3	319	63.9	379	75.9	–	–	406	81.2	437	87.4
3	CuS	410	82.0	323	64.7	270	54.1	220	44	–	–
4	As_2S_3	486	97.3	493	98.6	–	–	–	–	500	100

TABLE 3

Sorption of Neutral Red by Mercury Sulfide (II) in Relation to Aging of HgS and to the Time of Its Interaction with the Dye
Sorbent: 1000 mg/liter HgS; c_0 = 500 mg/liter (dye added after passage of H_2S): pH 0.52; t 28°. volume of solution 110 ml; precipitate shaken with solution for 20 minutes.

Experiment number	Aging time of HgS before addition of dye, in hours	Amount of dye sorbed c_0-c/m in relation to time of standing of the precipitate with solution before decantation					
		1/3 hour		24 hours		48 hours	
		in mg/g	in %	in mg/g	in %	in mg/g	in %
1	1/3	185	37	285	57	355	71
2	23	225	45	350	70	360	72
3	48	240	48	–	–	355	71
4	72	290	58	320	64	355	71
5	96	320	64	345	69	–	–

TABLE 4

Sorption of NeutralRed by Mercury Sulfide (II) in Relation to its Aging and Time of Interaction with the Dye
Sorbent: 1000 mg/liter HgS; c_0 = 500 mg/liter (dye added after passage of H_2S); pH 0.52; t 20°; volume of solution 110 ml; precipitate shaken with solution for 3 hours.

Experiment number	Time of aging of HgS before addition of dye, in hours	Amount of dye sorbed c_0-c/m in relation to time of standing of precipitate with solution before decantation			
		1/3 hour		24 hours	
		in mg/g	in %	in mg/g	in %
1	1/3	178	35.6	360	72.1
2	24	197	39.5	355	71.1
3	48	256	51.3	374	74.8
4	168	297	59.5	401	80.3

TABLE 5

Sorption of Neutral Red by HgS, CuS, and As_2S_3 in Relation to Time.
Sorbent: 1000 mg/liter of MeS or Me_2S_3; c_0 = 500 mg/liter (dye added after aging of sulfides); pH 0.52; t 28°; volume of solution 110 ml.

Experi-ment number	Metal sulfide	Amount of dye sorbed c_0-c/m after											
		1/3 hour		3 hours		24 hours		48 hours		96 hours		168 hours	
		in mg/g	in %	in mg/g	in %	in mg/g	in %	in mg/g	in %	in mg/g	in %	in mg/g	in %
1	HgS	–	–	178	36.6	197	39.5	256	51.3	–	–	297	59.5
2	CuS	360	72.1	–	–	319	63.8	196	39.2	193	38.6	160	32.1
3	As_2S_3	229	45.9	–	–	212	42.4	233	46.6	224	44.8	239	47.8

TABLE 6

Sorption Isotherm of NeutralRed by Cadmium Sulfide.
Sorbent: 1000 mg/liter CdS; t 28°; volume of solution 100 ml (dye added before passing H_2S); pH 0.52

Experiment number	Initial concentration c_0 of dye in mg/liter	Equilibrium concentration $\underline{c}$ of dye in mg/liter	Amount of dye sorbed $\frac{c_0-c}{m} = \frac{x}{m} = \Gamma$		Constant from the equation $y = kx^b$ for b = 1
			in mg/g	in %	
1	125	7	118	94.7	16.80
2	250	23	227	91.2	9.90
3	500	104	396	79.2	3.80
4	1000	283	713	71.3	2.50
5	1500	450	1050	70.0	2.30
6	2000	625	1375	66.9	2.20
7	2500	773	1727	69.2	2.24

The clearly defined sorption of neutral red which occurs during sulfide formation is immediately apparent from the results given in Table 1. It is most strongly expressed for As_2S_3, and is considerably weaker for HgS, PbS, SnS_2, and $3i_2S_3$. Intermediate values were obtained for CdS, Ag_2S, and Sb_2S_3.

Changes in sorption of the dye by the various sulfides during aging were of interest; for some of them, e.g. HgS, the process becomes stronger after 24 hours, for CuS – it becomes weaker –, while in the case of Ag_2S_3 there is no change in the amount of dye absorbed after this period has elapsed.

It is evident from Table 1 that it is possible to divide the hydrogen sulfide group of sulfides into three groups.

In subsequent experiments, carried out with the intention of getting a better defined picture of what goes on, changes in sorption of the dye over a longer aging period were studied. In addition to the three sulfides mentioned already (HgS, CuS, and As_2S_3), Sb_2S_3 was also used.

Experimental procedure was the same as before.

Results are tabulated in Table 2 and plotted on Fig. 1.

In these later experiments, the effect of the time factor on the amount of neutral red sorbed was shown more clearly. These results confirmed the interesting differences in this property of sulfides with aging.

It was of interest to study the sorption of neutral red in cases where it was added to precipitates which had already been formed and subjected to aging for various time intervals. It was possible, in this way, to find out whether changes occur in the sulfides during aging, or when they are under the influence of the dye. Experiments were carried out with HgS, CuS, and As_2S_3 with the difference that the precipitates which separated out were kept in the mother liquor for various time intervals, and, after addition of dye were shaken for 20 minutes. Afterwards, the residual neutral red was determined colorimetrically as usual.

Experiments were started with HgS; their results are given in Table 3 and plotted on Fig. 2.

The results given in Table 3 and Fig. 2 show that mercury sulfide (II) subjected to aging, absorbs neutral red to a large extent. On standing HgS (after aging) with a solution of the dye, its sorption increases, apparently, as a result of further de-aggregation of precipitate particles. This process is not so well defined in the case of mercury sulfide (II) precipitates which have been aged over a longer time period.

The experimental results given in Table 3 are the mean of 5-6 determinations which differ fairly appreciably from each other. Accordingly, in further experiments, time of shaking of precipitate with solution was increased to 3 hours.

Results are given in Table 4.

A comparison of results given in Tables 3 and 4 shows that analogous results are obtained in the case of precipitates which were shaken for 3 hours.

Results of experiments relating to the study of changes in sorption of neutral red by the sulfides HgS, CuS, and As_2S_3 with time are given in Table 5 and in Fig. 3.

The results given in Tables 2, 5, and Figs. 1 and 3 show that we have similar types of sorption curves for neutral red by the sulfides HgS, CuS, and As_2S_3, whether this dye has been added before formation of precipitates, or after they have separated out. Consequently, for this group of sulfides, the aging process is connected with the characteristic course of dye sorption.

In connection with the high sorption capacity of sulfides for neutral red, the question arises as to the size of the surface of the precipitates of these compounds and the reliability with which it can be determined by means of dye absorption. If it is assumed that a unimolecular layer is formed during sorption of neutral red, then it should be possible to calculate the surface area of precipitates.

The area occupied by a molecule of neutral red can be assumed to be roughly 100 A^2 on the basis of its structure. For an average amount of 300 mg of sorbed dye per g and a molecular weight of 288.8, the total number of molecules located on the precipitate surface will be given by $n = 0.3 \times 6 \times 10^{23}/288.8 = 6 \cdot 10^{20}$.

From which the surface area of the sulfide is given by:

$$\Sigma S = S \cdot n = 100 \cdot 10^{-16} \cdot 6 \cdot 10^{20} = 600 \cdot 10^4 \text{ cm}^2 \text{ or } 600 \text{ M}^2 \text{ per g of precipitate.}$$

These calculations show that sulfides have a large specific surface, comparable to that of activated charcoal. In using such a method for determining the surface area of a sorbent, it must be borne in mind that, for crystalline precipitates, determination of surface area on the basis of dye adsorption, as a comparison of this method with others shows, gives satisfactory results. Sulfides are more complex systems than crystalline precipitates, and particular care is necessary when their surface areas are to be determined by means of dyes. Nevertheless, it may be assumed that in the case of the formation of a unimolecular layer, or of surface chemical compounds on the surface, such a method, after further development, may be used for determining the surface area of sulfides.

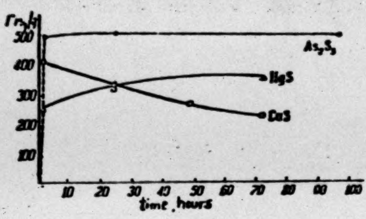


Fig. 1. Sorption kinetics of neutral red by the sulfides of HgS, CuS, and As_2S_3 (dye added before precipitate formation).

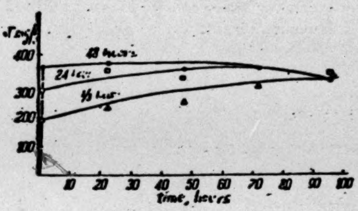


Fig. 2. Sorption kinetics of neutral red by mercury sulfide (II).

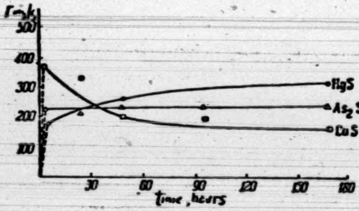


Fig. 3. Sorption kinetics of neutral red by HgS, CuS, and As_2S_3 (dye added after aging of precipitates for various time intervals).

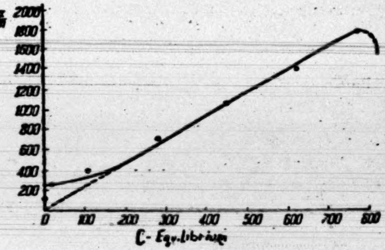


Fig. 4. Sorption isotherm of neutral red by cadmium sulfide.

Further experiments were carried out in order to explain, on the one hand, the character of the interaction of the surface active materials with sulfides (in this case, neutral red), and on the other — the structure of the three groups of sulfides indicated, and its change on aging.

It is possible to assess the character of the interaction of the dye with sulfides, to a certain extent, from the shape of the sorption isotherm; a study of the structure itself is conveniently realized by means of the electron microscope. Experiments were carried out along these lines too. CdS was chosen as a test object for determining the sorption isotherm.

Experiments were carried out as follows: Into a 150 ml flask were introduced a $CdCl_2$ solution (enough to give 0.1 g of CdS), various amounts of neutral red, HCl (1: 1), and water. HCl was added in an amount sufficient to make the solution 0.3 N, while water was sufficient to bring the volume up to 100 ml. The flask was placed in a thermostat operating at 28°; after 10 minutes, H_2S was bubbled through at the rate of 500 cm^3/minutes. When 5 minutes had elapsed, the flask was stoppered and shaken for 10 minutes. The precipitate of CdS was separated by centrifuging. The amount of dye remaining was determined colorimetrically as before.

Results are given in Table 6 and in Fig. 4.

Experiments were also carried out with high concentrations of neutral red (300, 400 mg/liter); these showed a sharp decrease in the amount of dye sorbed as compared with that formed in Experiment No. 7 (Table 6). Nevertheless, large deviations were obtained in parallel tests. It is possible that at a given dye concentration, the degree of aggregation increases rapidly, leading to poor reproducibility.

The results given in Table 6 and in Fig. 4, show that the distribution of dye between its aqueous solution and CdS is proportional to concentration over a wide range; the relation can be expressed with fair approximation

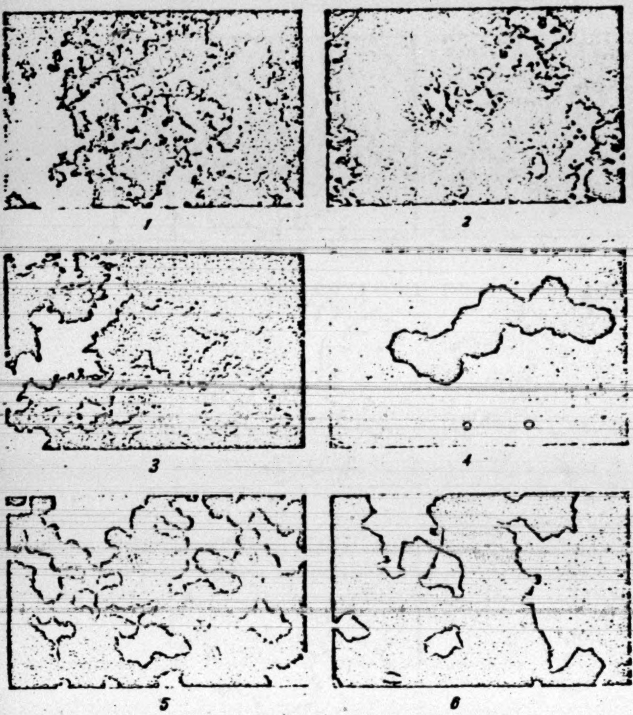


Fig. 5. Microphotographs of Sulfides: (magnification X 12,000).
1) SnS_2; 2) CuS; 3) Ag_2S; 4) CdS; 5) CdS; 6) PbS;

by the equation $y = Kx^b$, where $b = 1$, and $K = 2.3$. This points to a process of solution of the colloidally dispersed dye in the cadmium sulfide gel.

It is interesting that absorption of dye by cadmium sulfide is manifested to a strong degree, and, at its maximum at 0.69 mM CdS, 0.6 mM of neutral red is used — roughly equimolecular amounts.

Investigation of Sulfide Structure*

The surface area of the sulfides, and the character of this surface depend on the structure of the precipitates of these compounds. The electron microscope should therefore be very useful for studying the sorption of dyes by sulfides, and change of sorption with time.

Experimental Procedure

A 100 kV electron microscope — Type EM-100 — capable of giving a magnification of 12,000 was used. The resolvable distance was ~100 A, voltage 84 kV.

---

* This part of the work was carried out in Yu. M. Kushnir's laboratory by L. I. Zemlyanova to whom we are grateful.

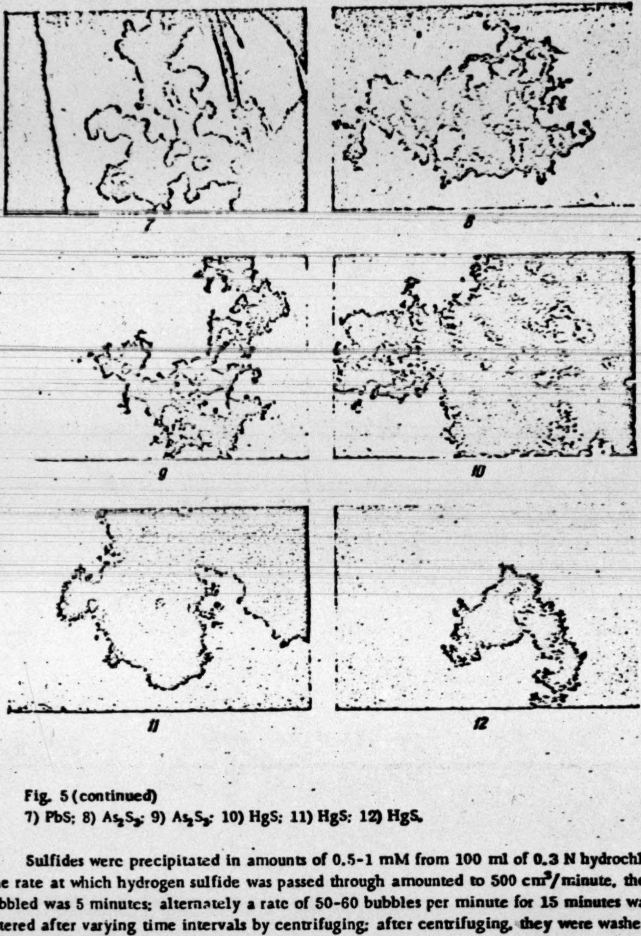

7 8 9 10 11 12

Fig. 5 (continued)
7) PbS; 8) As_2S_3; 9) As_2S_3; 10) HgS; 11) HgS; 12) HgS.

Sulfides were precipitated in amounts of 0.5-1 mM from 100 ml of 0.3 N hydrochloric acid solution at 25°. The rate at which hydrogen sulfide was passed through amounted to 500 cm^3/minute, the time for which it was bubbled was 5 minutes; alternately a rate of 50-60 bubbles per minute for 15 minutes was used. Precipitates were filtered after varying time intervals by centrifuging; after centrifuging, they were washed 4 times with distilled water and transferred to test tubes. The sulfides were kept under a layer of water in test tubes; the tubes were themselves stoppered.

Preparation of a sample for examination under the electron microscope was carried out as follows: After shaking the contents of the tube, a drop containing the sulfide in suspension was removed from inner part of the solution with a fine capillary; the drop was placed on a collodion film fixed on a nickel grating. 5-6 test samples which were taken in this way were then dried at 25°, and examined under the microscope.

The microphotographs thus obtained are shown on the enclosed plate. Photographs (1-12) were taken of the sulfides HgS, SnS_2, CuS, Ag_2S, CdS, PbS, and As_2S_3 aged for 2 and 24 hours. Microphotographs 8 and 10 are those of gels of As_2S_3 and HgS respectively examined 2 hours after preparation.

These microphotographs show that all the sulfides examined have a porous structure which means a high specific surface; at the same time, the sulfides differ appreciably amongst themselves with respect to structure. CdS and PbS have a crystalline structure; at low rates of formation, precipitates of these compounds consist of large sized particles (microphotographs 4, 6). It should be noted however, that the edges of CdS and PbS crystals are not sharply defined; this, apparently, is characteristic of sulfides prepared under analytical conditions, as distinct from typically crystalline precipitates.

Ag_2S is worthy of attention since it has a more compact structure than e.g. CuS, SnS_2, and As_2S_3, for which a friable, porous, structure of the gel is characteristic. It should be noted that Ag_2S has the least tendency to coprecipitate with metals of the III analytical group, as compared with all the sulfides of the hydrogen sulfide group. This tendency is not manifested with respect to its capacity to sorb neutral red. The sulfides HgS, SnS_2, CuS, and As_2S_3 differ amongst themselves with respect to the character of their aggregation, and the porosity of their particles.

Microphotographs 8 and 10 which represent freshly precipitated As_2S_3 and HgS gels respectively, allow them to be compared with the gels of the same compounds which have been allowed to age. It can be reckoned that As_2S_3 does not change its structure on aging. In the case of HgS however, as can be seen from microphotographs 10 and 11, considerable morphological changes occur in gel character on aging (after 24 hours). HgS is, apparently, an aggregate of fine crystals of granular structure, while a fresh gel of this sulfide has a denser structure; small, individual particles cannot be distinguished in it. While working with HgS, it was observed visually, that the flocs of HgS initially formed, break down after 24 hours into finer, individual, particles.

From what has been said, it can be concluded that, apparently, in the case of HgS, a process of de-aggregation of particles occurs (which increases its sorptive capacity). In the case of arsenic (III) sulfide however, as a result of the absence of structural change, the specific sorbing surface remains unchanged. This is also the case for particles having a crystalline structure, CdS and PbS, for which the processes of coagulation cannot be so sharply defined as for amorphous precipitates (e. g. Ag_2S and CuS). The process of aging of Ag_2S and CuS has not yet been studied with the aid of the election microscope; studies along these lines are continuing.

Thus, on the basis of the small amount of data obtained by application of the electron microscope to analytical precipitates, it is clear that this technique can be used successfully for studying aging of precipitates and those changes in structure and surface which occur during aging.

DISCUSSION OF RESULTS

Of the observations made during the present investigation, the most notable feature is the variation in behavior of sulfides towards sorption of neutral red which is observed during aging of the precipitates.

The compounds which we studied can be divided into three groups: I) HgS, Bi_2S_3, Sb_2S_3, SnS_2; II) CuS, Ag_2S; III) CdS, PbS, As_2S_3, according to whether, during aging, the amount of dye absorbed by them increases, decreases, or remains unchanged, respectively.

The experiments show that a study of the sorption kinetics of neutral red by the sulfides of mercury (II), copper (II), and arsenic (III) gives similar curves, apart from whether the dye is added before precipitation of a solid phase, or to a precipitate already formed. It is obvious that the aging process of the sulfides examined, and the structural changes which are observed during this process, proceed differently. Apparently, this may also apply to other sulfides, for which aging was only studied in the presence of the dye (See Table 1).

Metal sulfides belong to the group of precipitates for which clearly manifested aging is connected with a number of physical and chemical changes; these changes may be of great significance for the nature of sorption.

The physical changes include: particle aggregation, related to a decrease in the overall surface of the precipitates; growth of crystals and development of their form with a gradual change over from a disordely state to uniformly arranged structural units in space; polymorphic transformations which often occur in sulfides.

Chemical changes include conversion of sulfides into less hydrated forms. Their interaction with hydrogen sulfide is not excluded either.

The behavior of the sulfides of copper (II), and silver to dye sorption is easiest to explain. It is known from published data, that during aging of precipitates, aggregation of their particles occur with decrease in gel volume and total surface. We observed this process for the two sulfides indicated.

It is natural to assume in the case of CdS, PbS, and As_2S_3, which hardly change their capacity to absorb the dye on aging, that the effective sorbing surface remains practically the same, independently of the age of the sulfide gel.

The most difficult group to explain is the first one: HgS, Sb_2S_3, SnS_2, and Bi_2S_3. On the basis of hypothesis re surface interaction of sulfides with dyes, it is essential, in these cases, to assume de-aggregation of the unstable accumulation of particles formed initially, with an increase in total surface of the precipitate.

These ideas re the connection between the structure of the sulfides and their capacity to sorb neutral red, receive confirmation from electron microscope studies of the sulfides. Such studies showed that CdS and PbS have a crystalline structure (Microphotographs 4, 5, 6, 7), for As_2S_3 the gel has a net-like structure, and, apparently, the total surface area does not change on aging (Microphotographs 8 and 9). This agrees with the fact that the given sulfides, on aging, hardly affect the neutral red content of the solution. The surface of crystal precipitates of CdS and PbS does not change to any appreciable extent, as compared with that of amorphous precipitates (CuS, Ag_2S). The same is observed in the case of arsenic sulfide (III), as noted above.

Changes in the structure of CuS and Ag_2S with time was not studied. Electron microscope photographs of these sulfides show that they are accumulations of particles aggregated during their formation. The gel of Ag_2S has a particularly compact structure as compared with those of other sulfides.

It was visually observed, in the case of mercury sulfide (II), that the flocs originally formed, break into finer particles on aging. Increase in surface area of the precipitate, and an increase in the amount of dye sorbed during aging, are also connected with this process.

The mechanism of the interaction of sulfides with the dye we used is of very great interest. The fact that the amounts of neutral red sorbed, do not differ very much, whether the dye is added before or after precipitate formation, points to the very large surface area which the sulfide gels possess (see the account on p. 45 ff). Electron micrographs also testify to this; it is clear from them that the particle dimensions of, say, cadmium sulfide amounts to $\sim 5 \cdot 10^{-6}$ cm, i.e. values which correspond to a colloidal degree of dispersivity. It is also clear from them that the gels of As_2S_3, SnS_2, and CuS have a very porous structure, as well as the CdS gel (Fig. 5), the structural units of which are crystalline. It can be assumed that the skeleton of the As_2S_3 gel is more stable than those of CuS and Ag_2S, as a result of which, its physical structure and its internal sorbing surface do not change appreciably on aging. On the other hand, CuS and Ag_2S gels acquire a high density, with a smaller number of interstices between individual particles, on aging. The neutral red sol diffuses in the sulfide gel and is sorbed by the inner surface. The negative charge of sulfides and positive charges of the neutral red sol permit one to assume that diffusion of the dye is caused by an electrostatic interaction between these particles; this, apparently, is the first stage of the process. The shape of the sorption isotherm of neutral red by cadmium sulfide is of interest from this point of view. The relation between amount of dye added, and that absorbed by the solid phase enables one say that, in the given case, a process of colloidal solution is taking place during dispersion of neutral red in cadmium sulfide.

Using the experimental evidence set out in the present article, it is possible to consider the part played by the surface of sulfides during coprecipitation with various other metals, primed with a number of new facts. First of all, it should be noted that the surface of various sulfides differ very little from one another; the small differences in the amount of dye absorbed testifies to this. On the other hand, on aging of these precipitates, a completely different state of affairs is obtained with respect to these surfaces, and this, undoubtedly, affects coprecipitation.

The structure of the precipitates, on which the size of the surface depends, is of importance in coprecipitation. A comparison of electron micrographs of Ag_2S with those of other sulfides, demonstrates clearly the large difference in precipitate structure. Experiments show that silver sulfide possesses only an insignificant capacity to attract the various metals of the third group; this may be explained by the compact structure of its gel. The relation between extent of coprecipitation and sulfide structure is also clear from the fact that during rapid saturation of solution with hydrogen sulfide, with consequent increasing dispersivity of CdS, capture of zinc by this precipitate increases rapidly (Microphotograph 5).

The results of the present investigation show that accumulation of experimental data, along the lines considered, should lead to a better understanding of the coprecipitation which occurs during precipitation of sulfides.

In conclusion, we wish to express our sincere thanks to Corresponding Member of the USSR Academy of Sciences I. P. Alimarin for directing this work.

SUMMARY

1. A study of the sorption kinetics of neutral red by sulfides, has shown that these compounds can be divided into three groups according to the path followed by the process: I) HgS, Bi_2S_3, Sb_2S_3, SnS_2; II) CuS, Ag_2S; III) CdS, PbS, As_2S_3. In the first group, dye sorption increases on aging of the precipitate, in the second – it decreases, while in the third – it remains unchanged.

2. It has been shown that the path taken by sorption of neutral red by the sulfides of mercury (II), copper (II), and arsenic (III) does not depend on the order in which the dye is added (aging in the presence of neutral red or without it). This indicates that the presence of the dye does not affect the character of the aging process of these sulfides.

3. It has been suggested that the decrease, or increase, in capacity to sorb the dye, which is observed during aging of sulfides depends on aggregation or de-aggregation of precipitate particles. The absence of changes in the amount of sorbed dye is determined by the stable structure of the sulfide gel, as a result of which, the specific sorption surface hardly changes during aging.

4. The sorption isotherm of neutral red by cadmium sulfide may be expressed by the equation: $y = Kx^b$, where $b = 1$, and K has a constant value of 2.3, over a wide concentration range for the dye. This indicates a process of colloidal solution of dye on its dispersion in CdS.

5. A study of the gels of the sulfides Ag_2S, SnS_2, CuS, As_2S_3 and Sb_2S_3 by means of the electron microscope has shown that they have a porous, cellular, structure. Ag_2S has a denser structure than the others. PbS and CdS have crystalline structures.

6. On the basis of the results obtained a hypothesis is advanced for the mechanism of interaction of neutral red with sulfides.

Received October 30, 1956

LITERATURE CITED

[1]. S. Linder, and H. Picton, J. Chem. Soc., 61, 120 (1892).

[2] I. Kolthoff, E. Pearson, J. Phys. Chem., 36, 549 (1932).

[3] I. Kolthoff, R. Moltzan, J. Phys. Chem., 40, 779 (1936).

[4] I. Kolthoff, and F. Griffith, J. Phys. Chem., 42, 53 (1938).

[5] N. A. Rudnev, J. Anal. Chem., 8, 1, 3 (1953) (T. p. 1)*.

[6] I. P. Alimarin, N. A. Rudnev, and L. I. Guseva, Collection "Application of Marked Atoms in Analytical Chemistry". Acad. Sci. Press, Moscow, 1955.

[7] N. A. Rudnev, J. Anal. Chem., 10, 4, 217 (1955) (T. p. 203)*.

[8] H. Picton and S. Linder, J. Chem. Soc., 71, 568 (1897).

[9] W. Biltz, Ber., 37, 1095 (1904).

[10] H. Rheinbold and E. Wedekind, Kolloidchem. Beihefte, 17, 118 (1923).

[11] A. M. Koganovsky, Colloid J., 11, 237 (1949).

[12] A. M. Koganovsky, Colloid J., 11, 417 (1949).

[13] N. S. Sheinker, J. Phys. Chem., 4, 6, 865 (1933).

[14] N. S. Sheinker, J. Phys. Chem., 4, 6, 861 (1933).

---

* T. p. = C. B. Translation pagination.

[15] E. Peneth, Z. Electrochem., 28, 113 (1922).

[16] V. G. Khlopin and M. S. Merkulova, J. Phys. Chem., 13, 9, 1982 (1939).

[17] I. Kolthoff and C. Rosenblum, J. Am. Chem. Soc., 55, 2656 (1933).

[18] I. Kolthoff, and C. Rosenblum, J. Am. Chem. Soc., 55, 2664 (1933).

[19] E. N. Slovnova, Author's Thesis, Moscow, 1954.

[20] V. I. Kuznetsov, Prog. Chem., 18, 1, 75 (1949).

[21] K. Fajans, O. Hassel, Z. Electrochem., 29, 495 (1923).

[22] N. P. Rudenko, J. Russ. Phys. Chem. Soc., 62, 3, 505 (1930).

THE METHOD OF "IN SITU NASCENDI" REAGENTS FOR DETERMINATION OF THE ALKALINE EARTH METALS

A. P. Terentev, E. G. Rukhadze, and K. I. Litvin

The M. V. Lomonosov Moscow State University and the Stalin Mining Institute, Moscow

Organic reagents which are widely used at present for quantitative gravimetric analysis, normally, interact directly with the ion of the element to be determined, and form a slightly soluble inner complex, a complex compound, an addition product, or a slightly soluble salt. The effect of organic reagents is not exhausted in these reactions however.

From published results it is clear that during recent years other compounds have started to find use for analytical studies: these compounds themselves however do not form a precipitate with the test ion, but only indirectly affect the precipitation process, and favor precipitation of a slightly soluble compound.

Ostroumov [1], on the basis of a large amount of experimental data made a number of theoretical generalizations, and gave an overall picture of the interaction of pyridine, α-picoline, hexamethylenetetramine, and urea with solutions of metal salts. The author, on the basis of a fair amount of evidence, shows what wide possibilities are opened up by the use of organic bases in quantitative gravimetric analysis. With the introduction of organic amines into practice, it has been possible to develop new methods for determining iron, aluminum, chromium, titanium, zirconium, scandium, indium, gallium, beryllium, etc., and methods of separating these metals from each other.

Flaschka and Jakobljevich [2], using experimental results obtained by Barber and Grzeskowiak [3], successfully used thioacetamide for quantitative determination of antimony, bismuth, molybdenum, copper, and arsenic. Taimni and Agarwal [4], by means of thio salts, developed a method for complete and rapid precipitation of molybdenum and platinum, and also developed methods for determining arsenic, selenium, tellurium, and tin.

Musil, Gagliardi, and Reische [5, 6], used thioformamide for separating arsenic, antimony, and tin. Bloemendal and Veerkamp [7], used various organic sulfides in qualitative analysis, substituting them for hydrogen sulfide and ammonium sulfide. Pilz [8], determined manganese and separated it from calcium and magnesium by means of trithiocarbonic acid. Wiberg and Bauer [9], used ammonium thiocarbamate for precipitating metals of the hydrogen sulfide group. Hummel and Sandell [10], separated alumium and iron ions with thioglycollic acid.

Willard [11], has pointed out the possibility of the wide use in gravimetric analysis of such organic compounds as methyl oxalate, dimethyl sulfate, diethyl sulfate, methyl ethyl sulfate, triethyl phosphate, sulfamic acid, acetamide, tetrachlorophthalic acid, and urea. The author and his coworkers [12], who successfully used some of the compounds listed as reagents for quantitative precipitation, and separation, of a number of elements, called this method "precipitation from homogenous solution". Thus, Elving and Van-Att [13], determined alkaline earth elements with dimethyl sulfate. Gordon, Reimer, and Burtt [14], studied the distribution of strontium in barium sulfate during precipitation from a homogeneous solution. Gordon and Wroczynski [15], precipitated calcium quantitatively with diethyl oxalate. Wagner and Wuellner [16], precipitated barium with sulfamic acid. Elving and Zook [17], proposed a method for quantitative separation and determination of lead in milligram amounts by precipitation with dimethyl sulfate. Willard and Gordon [18] precipitated the basic sulfate of quadrivalent tin with urea. Gordon, Reimer, and Teicher [19] precipitated tin in the presence of manganese with urea, and barium in the presence of strontium, with dimethyl sulfate. Weaver [20] had indicated the possibility of fractional separation of rare earths by precipitation with methyl oxalate. Gordon and Shaver [21], have separated several pairs of rare earths, by precipitation from homogeneous solutions of the complex compounds of their oxalates with ethylene-diaminetetracetic acid. Stine and Gordon [22] have proposed a method of determining the thorium content of Monazite sand, based on precipitation of throium iodate from homogeneous solutions.

Willard [23]. has determined cerium as the iodate by precipitation from a homogeneous solution, and separated it from other rare earths.

All the organic compounds enumerated above, which have been used for quantitative precipitation of metals, have one property in common: being in solution, they supply precipitant ions to the solution under various conditions. This article is devoted to: a search for a reagent of this kind; the development on the basis of such a reagent of a new method, that of "in situ nascendi" reagent – precipitants, for determination and separation, with the use of masking agents, of the alkaline earths; and, finally, the study of the mechanisms of these "in situ nascendi" reagent-precipitants.

Principles of the Method of "In situ nascendi" Reagents.

Mechanism of the Action of Organic Compounds which Supply Precipitant Ions

It is well known from gravimetric practice that the particle dimensions of a precipitate depend on the conditions under which precipitation is carried out. It is essential to remember that the rates of aggregation and orientation respectively, should be such as to favor formation of large crystals. It is obvious that if precipitant ions are not added to the test solution directly, but conditions can be found under which they are gradually formed in the solution which contains the ion to be determined, at such a rate, that precipitation occurs through all the volume, slowly and uniformly, then the slow growth of crystals and their correct formation will lead to minimum occlusion. Moreover, the total surface area of the crystals obtained will also be less because of their large size, and this in turn, will probably lead to a decrease in adsorption.

Methods of precipitation where precipitant ions are formed in solution, have been used for a long time, in analytical chemistry. E.g. the classical method of determining calcium by precipitating it from acid solutions with ammonium oxalate, and also of magnesium with ammonium phosphate, with subsequent addition of ammonia, is carried out in such a way that on changing the pH of the solution by addition of ammonia dropwise, we gradually "obtain" the requisite precipitating ions $C_2O_4^{2-}$ and PO_4^{3-}, to give precipitates which can then be filtered. But the best results are obtained by using organic compounds which are capable of supplying precipitant ions; e.g. dimethyl sulfate or dimethyl oxalate, under certain conditions, gradually supply the precipitant ions SO_4^{2-} and $C_2O_4^{2-}$ respectively. By regulating the amount of SO_4^{2-} and changing the pH of the medium, we can separate slightly soluble compounds which are in a form suitable for filtration etc. Thus, the question really boils down to, in particular, a choice of "in situ nascendi" precipitant ions as a method of getting pure precipitates during gravimetric determination of the elements. In this sense, we reckon that the terminology current in foreign literature "precipitation from homogeneous solution" is not very appropriate, since, as soon as the reagent has been added, a precipitant ion is formed, which forms a precipitate, i.e. we have a heterogeneous system during the precipitation process.

If it should be possible to choose conditions such that the rate at which precipitant ions become available can be controlled, then it is obvious that not only precipitation of any particular ion with a view to its determination can be effected, but that practically complete separation of a number of ions, whose solubility products differ, should be possible. Consequently, the method of "in situ nascendi" reagents is also a method leading to more complete separation of the elements.

The Use of "In situ nascendi" Reagents for Determining Barium, Strontium, and Calcium

Hitherto we have not had at our disposal sufficiently reliable organic reagents for determining alkaline earths, or methods of separating them from each other. A huge amount of experimental data has been accumulated by chemists, and a large number of papers published on the determination of alkaline earths, chiefly, by means of inorganic reagents. E. g. the generally adopted classical method of determining barium by precipitation as barium sulfate has a few disadvantages; viz. it takes a long time, finely dispersed precipitates are formed, and it is difficult to separate barium sulfate in a pure state because of coprecipitation [24]. Determination of barium in the presence of strontium and calcium has never been achieved. Quite a few papers [25-35] have been devoted to the causes of adsorption, and to the preparation of extremely pure barium sulfate precipitates; nevertheless all attempts to eliminate absorption by $BaSO_4$, . and to speed up its determination by means of inorganic reagents have, hitherto, been unsuccessful [36]. Separation of barium as sulfate remains the least accurate determination in quantitative analysis. In view of this, it has been suggested [37]. that empirical corrections be applied to experimental results. Calcium, precipitated as the oxalate with inorganic reagents, does not separate out in a pure state either. A large number of methods have been suggested [38-40]. for precipitating very pure calcium oxalate, but it has proved impossible to eliminate coprecipitation completely.

TABLE 1

Determination of the Alkaline Earths by Dimethyl Sulfate in Aqueous-Methanol Solution

Cation determined	Cation taken in mg	Cation found in mg	Error in mg	Error in %
Ca^{2+}	51.40	51.58	+ 0.18	+ 0.3
Ba^{2+}	6.90	6.82	−0.08	−1.1
	34.51	34.00	−0.51	−1.54
	69.05	69.20	+ 0.15	+ 0.20
Sr^{2+}	10.23	10.14	−0.09	−0.8
	10.23	10.18	−0.05	−0.40

Accordingly, we were very interested in Elving and Van-Att's method [13] of determining barium, strontium, and calcium with dimethyl sulfate. These authors precipitated the alkaline earths as sulfates from aqueous-methanol solutions by means of dimethyl sulfate. We checked this method and were convinced that it gives good results. In this method it is not necessary to allow precipitates to stand for long: determination of barium, strontium, and calcium (separately) takes 3 hours; the precipitates obtained separate out in a coarsely dispersed form which is easy to filter and can be washed rapidly (Table 1).

All the same, the method suggested by these authors [13], has a number of fairly appreciable drawbacks, some of which we were able to eliminate. According to their procedure, sulfate precipitates are allowed to stand in open beakers in a water bath. The reaction mixture contains dimethyl sulfate and methanol, the vapors of which are poisonous. Moreover, in order to keep the volume of solution constant, it is suggested that losses of methanol should be made up by adding fresh portions of this solvent from time to time. We avoid this evaporation of methanol very simply: a round bottom flask containing cold water + ice is fitted snugly over the beaker in which the reaction is carried out. This simplified reflex condenser practically completely stops evaporation of methanol and dimethyl sulfate.

It is still better to do away with methanol; we accordingly used glycerol instead of it.

Precipitation Procedure

Barium was determined as follows: to a solution containing 10-70 mg barium was added 5-15 ml glycerol, and the solution diluted to 50-100 ml with distilled water; 5 ml of dimethyl sulfate (it is best to use freshly distilled dimethyl sulfate, boiling point 188°, sp.gr. 1.332 at 20°) was then added dropwise. The solution plus precipitate formed was heated for 30 minutes in a water bath, when the compact, coarsely crystalline, precipitate of barium sulfate which thereby formed was filtered through an ashless paper (diameter 7 cm, blue ribbon quality), washed with water, dried, calcined at a red heat, and weighed as $BaSO_4$. It is possible to filter the precipitate through a sintered glass crucible and heat to constant weight at 140-160°.

The results obtained are given in Table 2 which includes the most characteristic results from parallel experiments.

TABLE 2

Determination of Barium with Dimethyl Sulfate in Aqueous-Glycerol Solution

Cation determined	Cation taken in mg	Cation found in mg	Error in mg	Error in %
Ba^{2+}	13.80	13.83	+ 0.03	+ 0.2
	20.30	19.56	−0.74	−1.7
	34.51	34.42	−0.09	−0.2
	34.30	34.54	+ 0.24	+ 0.6
	69.05	69.44	+ 0.39	+ 0.5

It is clear from Table 2 that the results of precipitation of barium from 5-15% aqueous-glycerol solutions with dimethyl sulfate is no less accurate than those obtained when precipitation is carried out from aqueous-methanol solutions. The barium sulfate precipitate separates out readily, and its coarse dispersion is easily detached from beaker walls. The "ripening" process is fairly rapid, 30-40 minutes, against the 6-12 hours taken for ordinary classical methods of precipitating barium in the cold.

Of interest is the determination of barium in the presence of other ions and acids, and in synthetic mixtures.

It is known from published results [34, 43], that determination of barium in the presence of NO_3^-, ClO_3^-, NO_2^- etc. does not give accurate results, and necessitates removal of these ions. Rudnev [41], points out that on precipitating barium in the presence of 0.05-0.5 N nitric acid, the weight of $BaSO_4$ precipitate increases by 1-7%

TABLE 3

Determination of Barium with Dimethyl Sulfate from 5-15% Aqueous-Glycerol Solutions, in the Presence of Other Ions and Acids

Barium taken in mg	Impurity added	Amount of impurity taken in mg	Error in mg	Error in %
13.80	Fe^{3+}	45.72	−0.03	−0.21
13.80		111.80	−0.03	−0.21
69.02		79.20	+ 1.06	+ 1.53
13.80	K^+	5.00	−0.15	−1.08
69.02		25.00	+ 0.31	+ 0.44
13.80		100.00	−0.09	−0.65
69.03	Na^+	18.85	+ 0.47	+ 0.68
69.03		94.25	−0.18	−0.26
13.80	Al^{3+}	10.00	−0.15	−1.08
34.51		500.00	+ 0.41	+ 0.12
13.80	Mg^{2+}	5.00	+ 0.09	+ 0.65
20.71		50.00	+ 0.12	+ 0.58
13.80	NH_4^+	25.00	+ 0.26	+ 1.88
69.03		630.00	−0.24	−0.34
13.80	Cr^{3+}	50.00	−0.21	−1.5
34.51		250	+ 0.32	+ 0.90
69.03	ClO_3^-	50.00	+ 0.41	+ 0.59
13.80		200.00	−0.09	−0.65
69.03	NO_3^-	50.00	+ 0.47	+ 0.68
13.80	NO_2^-	25.00	−0.03	−0.21
13.80	HCl	108.00	−0.03	−0.21
34.51	HNO_3	126.00	−0.14	−0.40
69.03	H_3PO_4	250.00	+ 0.06	+ 0.10
13.80		50.00	+ 0.14	21.00

TABLE 4

Determination of Barium (in Synthetic Mixtures) with Dimethyl Sulfate from 15% Aqueous-Glycerol Solutions

Barium taken in mg	Amount of impurity added in mg						Barium found	
	Al^{3+}	Fe^{3+}	Mg^{2+}	Na^+	K^+	Ca^{2+}	Error in mg	Error in %
13.80	50	50	100	100	100	130.0	+1.1	+4.0
103.55	50	50	100	100	100	130.0	+4.55	+4.0
55.22	10	15	10	10	10	10.02	+0.02	+0.3

TABLE 5

Determination of Alkaline Earths with Sodium Sulfamate ($C_6H_5NHSO_3Na$) in a Methanol Medium

Cation determined	Cation taken in mg	Cation found in mg	Error in mg	Error in %
Ba^{2+}	34.51	35.07	+ 0.56	+ 1.6
	13.80	14.06	+ 0.26	+ 1.9
Sr^{2+}	51.40	50.56	−0.84	−1.6
	20.86	20.41	−0.15	−0.7
Ca^{2+}	64.25	64.30	+ 0.05	0

TABLE 6

Determination of Alkaline Earths with Sodium p-Tolylsulfamate ($CH_3C_6H_4NHSO_3H$) in a Methanol Medium

Cation determined	Cation taken in mg	Cation found in mg	Error in mg	Error in %
Ba^{2+}	34.51	35.25	+ 0.74	+ 2.14
Sr^{2+}	51.40	52.29	+ 0.79	+ 1.54
Ca^{2+}	64.25	64.76	+ 0.51	+ 0.79

TABLE 7

Determination of Barium with Dimethyl Sulfate from 5-15% Aqueous-Glycerol Solutions in the Presence of Calcium Ions

Barium introduced in mg	Calcium introduced in mg	Barium found in mg	Error in mg	Error in %
13.80	64.20	14.06	+ 0.26	+ 1.4
13.80	25.68	13.83	+ 0.03	+ 0.21
7.30	64.20	7.41	+ 0.11	+ 1.4
69.90	12.84	69.79	−0.11	−0.1

and more. Karaoglanow [42], has shown that if $BaSO_4$ is determined in the presence of hydrochloric acid, the results obtained are too high by a few per cent. Fe^{3+}, and Cr^{3+} etc. interfere with barium determination [24, 44].

We have established experimentally that dimethyl sulfate precipitates relatively pure barium sulfate from solutions of barium chloride containing K^+, Na^+, NH_4^+, Al^{3+}, Cr^{3+}, Fe^{3+}, ClO_3^-, NO_3^-, NO_2^- and other ions; the precipitate formed being free from appreciable amounts of the ions listed.

TABLE 8

Determination of Barium in the Presence of Calcium and Strontium by Precipitation of Barium with Dimethyl Sulfate from a 20% Sugar Solution

Amounts in solution, in mg, in the presence of lactose			Barium found,	Amounts in solution, in mg, in the presence of glucose			Barium found,	Amounts in solution, in mg, in the presence of saccharose			Barium found,
Ba^{2+}	Sr^{2+}	Ca^{2+}	% error	Ba^{2+}	Sr^{2+}	Ca^{2+}	% error	Ba^{2+}	Sr^{2+}	Ca^{2+}	% error
34.52	51.40	177	+ 0.9	34.52	51.40	128.4	+ 6.0	34.52	51.40	177	−0.4
34.52	102.80	354	−1.4	34.52	51.40	256.8	+ 3.0	34.52	51.40	−	−5.0
13.81	51.40	177	+ 2.5	13.81	51.40	128.4	+ 5.1	13.81	51.40	−	−3.7

TABLE 9

Comparative Determination of Barium Precipitated in the Presence, and Absence, of Glucose as a Masking Agent

Taken in mg			Ba^{2+} found in the absence of a masking agent		Ba^{2+} found in the presence of glucose as a masking agent	
Ba^{2+}	Sr^{2+}	Ca^{2+}	in mg	% error	in mg	% error
20.71	102.80	354.00	23.88	+ 15	20.42	−1.4
34.51	51.40	354.00	30.36	−12	35.37	+ 2.5
34.51	102.80	88.50	33.13	− 4	34.84	+ 0.9

In addition, it was established that when 203.32 mg of Ba^{2+} was determined in the presence of 50 mg Fe^{3+} by precipitation with dimethyl sulfate, 202.38 mg of Ba^{2+} was recovered; this amounts to an error of −0.96 mg or −0.4%; on precipitation of the same amount of barium with sulfuric acid, 206.03 mg Ba^+ was found, i.e. the error was + 2.61 mg or + 1.7%.

Tables 3 and 4 contain results on the determination of barium with dimethyl sulfate from 5-15% solutions of glycerol in water, in the presence of alkali metals, divalent and trivalent metals, anions, and acids.

These experiments demonstrate fairly convincingly the advantages of organic compounds which can supply precipitant ions. The method of "in situ nascendi" reagents speeds up and makes the method considerably more accurate. Thus, if errors connected with coprecipitation of iron with $BaSO_4$, when the latter is precipitated with an inorganic reagent, are to be eliminated, it is necessary first of all to remove Fe^{3+} from barium by a double precipitation with ammonia, followed by removal of ammonium salts from solution. When, however, Ba^{2+} is precipitated with dimethyl sulfate, there is no need for a long separation operation, and barium can be precipitated with dimethyl sulfate in the presence of "interfering" ions: NO_3^-, ClO_3^-, Fe^{2+}, Fe^{3+}, Cr^{3+}, etc.

Other organic compounds were tried as precipitants in addition to dimethyl sulfate; these included: sodium sulfamate, and sodium p-tolylsulfamate which can also supply precipitant ions.

Barium precipitation was carried out under the same conditions as with dimethyl sulfate (Tables 5 and 6).

Despite the fact that the error percent was somewhat higher than when precipitation was effected with dimethyl sulfate, the use of these reagents may be justified since they are not so poisonous as dimethyl sulfate.

Determination of Barium, Strontium, and Calcium When Present Together

As pointed out before, the slow and uniform rate at which precipitant ions are made available in solution, coupled with the use of masking agents for complexing interfering ions, can be used for quantitative separation of elements on the basis of differences in their solubility products. With this end in view experiments were carried out on the determination of barium in a mixture of alkaline earths.

We established in preliminary experiments that in aqueous-glycerol media, calcium is not precipitated by dimethyl sulfate even on heating and long standing. Addition of large amounts of alcohol in the presence of glycerol, similarily, did not lead to precipitation of calcium sulfate. Even addition of moderate amounts of dilute sulfuric acid did not lead to precipitate formation. We used this fact for determining barium in the presence of calcium. Table 7 contains results of determinations of Ba in the presence of Ca by precipitation with dimethyl sulfate from 5-15% aqueous glycerol solutions. Precipitation of Ba was carried out under the same conditions as described above. The data of Table 7 show that Ba can be completely determined in presence of Ca if precipitation of barium sulfate is carried out with dimethyl sulfate from 5-15% aqueous-glycerol solution. We were unable however to determine Ba in the presence of Sr and Ca under the same conditions. A sugar (lactose, glucose, saccharose) solution proved to be the most suitable masking agent in this case. Determination of Ba in a solution containing Sr and Ca was carried out as follows: to a solution containing 20-35 mg Ba, 177-354 mg Ca, and 51.4-102.80 mg Sr, was added 10 ml of 20% sugar solution; water was added to the solution to make it up to 100 ml and then the whole was heated for 5-10 minutes on a boiling water bath, finally, 5 ml of dimethyl sulfate was added. After 25-30 minutes the precipitate was filtered through an ashless paper, washed with water, dried, calcined, and weighed. Experimental results are given in Table 8.

Table 9 contains comparative results for precipitation of barium with dimethyl sulfate from solutions containing strontium and calcium, both in the presence, and absence, of a "masking agent" — glucose.

These experimental results show that the proposed method can be used for the determination of barium in solutions containing appreciable amounts of strontium and calcium.

On the other hand, we have not yet succeeded in separating such pairs as calcium and strontium, and barium and strontium.

SUMMARY

1. The principles and advantages of the method of "in situ nascendi" reagents are outlined. By using organic compounds which gradually form precipitant ions during the reaction, it is possible to get precipitates which contain a minimum of coprecipitated impurities.

2. Dimethyl sulfate, phenol, sodium sulfamate, sodium p-tolylsulfamate can be used as reagents for the alkaline earths Ba^{2+}, Sr^{2}, and Ca^{2+}.

3. The fundamental principles of the method of "in situ nascendi" reagents are set out and it is shown experimentally that organic compounds which can supply precipitant ions, possess considerable advantages, as compared with inorganic reagents, for determination of the alkaline earths.

4. Methods based on "in situ nascendi" reagents have been developed for the determination of barium, strontium, and calcium, and also for determining barium in the presence of strontium and calcium.

The method is simple and ensures reliable results. The method is as accurate as existing chemical methods, and is appreciably faster than these.

Received May 25 , 1955

LITERATURE CITED

[1] E. A. Ostroumov, "New Methods of Chemical Analysis Involving the Use of Organic Bases", State Geol. Press, 1952.

[2] H. Flaschka, and H. Jakobljevich, Anal. Chem. Acta. 4, 247 (1950); ibid, 4, 351 (1950); ibid, 4, 356 (1950); ibid, 4, 482 (1950); ibid, 486 (1950).

[3] H. H. Barber and E. Grzeskowiak, J. Anal. Chem., 21, 192 (1949).

[4] J. K. Taimni, R. P. Agarwal, Anal. Chem. Acta. 9, No. 2, 116 (1953); ibid, 9, No. 3, 203 (1953).

[5] A. Musil, E. Gagliardi and K. Reische, Z. anal. Chem., 137, No. 4, 252 (1952).

[6] A. Musil, E. Gagliardi and K. Reische, Z. anal. Chem., 140, No. 5, 342 (1953).

[7] H. Bloemendal, T. A. Veerkamp, Chem. Weekblad, 49, No. 9, 28/II, 147, (1953).

[8] W. Pilz, Mh Chem., 33, No. 6, 1291 (1952).

[9] E. Wiberg, R. Bauer, Angew. Chem., 64, No. 9-10, 270 (1952).

[10] R. A. Hummel, E. B. Sandell, Anal. Chem. Acta, 7, No. 4, 308 (1952).

[11] H. H. Willard, Anal. Chem. (U.S.), 22, No 11, 1372 (1950); Fresenius Brigit, Chem. Labor. und Betrieb No. 6, 299 (1953); Russian Abstracts (Chem.), No. 23, 188 (1954). -

[12] L. Gordon, C.C. Reimer and H. Teicher, Anal. Chem. (U.S.), 25, 838 (1953).

[13] P. I. Elving, and K. E. Van-Att, Anal. Chem. (U.S.), 222, 1375 (1950).

[14] L. Gordon, C. C. Reimer and B. B. Burtt, Anal. Chem. (U.S.), 26, 842 (1954).

[15] L. Gordon, A. F. Wroczynski, Anal. Chem. (U.S.), 24, 896 (1952).

[16] W. F. Wagner, and I. A. Wuellner, Anal. Chem. (U.S.), 24, 1031 (1952).

[17] P. J. Elving and W. Zook, Anal. Chem. (U.S.), 25, 502 (1953).

[18] H. H. Willar, and L. Gordon, Anal. Chem. (U.S.), 25, 170 (1953).

[19] L. Gordon, C. Reimer and H. Teicher, Anal. Chem. (U.S.), 25, 838 (1953).

[20] B. Weaver, Anal. Chem. (U.S.), 26, 479 (1954).

[21] L. Gordon and K. J. Shaver, Anal Chem. (U.S.), 25, 784 (1953).

[22] C. R. Stine and L. Gordon, Anal. Chem. (U.S.), 25, 1519 (1953).

[23] H. H. Willard, Anal. Chem. (U.S.), 25, No. 11, 1954 (1953).

[24] I. M. Kolthoff and E. B. Sandell, "Quantitative Analysis", State Chem. Press, 1948, pp. 118, 344.

[25] F. Hohn and R. Otto, Z. anal. Chem., 126, 257 (1923).

[26] J. Kolthoff, M. Cittert, Z. anal. Chem., 63, 392 (1923).

[27] V. Njegovan, and V. Marjonovie, Z. anal. Chem., 73, 271 (1928); 74, 191 (1928).

[28] J. Johnston and L. Adams, J. Am. Chem. Soc., 33, 529 (1911).

[29] T. Richards, H. Parker, Z. anorg. Chem., 8, 419 (1895).

[30] E. Allen and I. Johnston, J. Am. Chem. Soc., 32, 528 (1910).

[31] J. Johnston and L. Adams, J. Am. Chem. Soc., 33, 829 (1911).

[32] S. Popoff and E. Neumann, Ind. Eng. Chem., 2, 45 (1930).

[33] E. Hintz and H. Weber, Z. anal. Chem., 45, 31 (1906).

[34] H. Weiser, and S. Sherrik, J. Phys. Chem., 23, 205 (1919).

[35] N. Ushakov, "Dispersivity of Analytical Precipitates". Moscow State University Thesis, 1949.

[36] Masaji Miura, J. Sci. Hiroshima Univ, A, 16, No. 3, 551 (1953).

[37] C. Waters, Bur. Standards, Tech. Paper, No. 177, p. 25.

[38] J. Kolthoff and E. Sandell, J. Phys. Chem., 37, 448 (1932).

[39] H. Chapman, Soil Sci., 26, 479 (1928).

[40] E. Sandell, J. Kolthoff, Ind. Eng. Chem., Anal. Ed., 11, 90 (1939).

[41] N. A. Rudnev, Scientific Proceedings of Kazan University, Vol. 40, 6, 1054 (1930).

[42] Karaoglanow, Z. anal. Chem., 56, 241 (1917).

[43] Masaji Miura, J. Sci. Hiroshima Univ., A, 16, No. 3, 563, (1953); ibid., A, 17, No. 1, 161; ibid., A, 17, No. 1, 167.

[44] O. P. Syzganova, Trans. Kazan Chem. Tech. Inst., No. 17, 139 (1952).

OSCILLOGRAPHIC POLAROGRAPHY ON SOLID ELECTRODES

I. I. Tsapiv

Lvov Polytechnical Institute

The use of the cathode ray oscillograph for polarographic purposes is attracting the attention of many investigators these days. A proof of this, is the appearance, both in Soviet as well as in foreign chemical journals, of papers devoted to this question. In all these papers, both in the earliest — Matheson and Nichol [1], and the most recent — Gokhshtein and Surkov [2], the ordinary polarograph circuit with a dropping mercury electrode was employed as the polarographic cell. Schemes have also been suggested in which a streaming electrode is used (Heyrovsky's scheme [3]).

Taking into account the difficulties which crop up during the use of mercury electrodes, e.g. instability of the oscillographic image, caused by the process of drop formation, the poisonousness of mercury, etc., the use of solid metal electrodes in oscillographic polarography is of undoubted interest. This question is becoming more pertinent, since solid electrodes are beginning to take a more prominent part in ordinary polarography, and, in many cases replacing the dropping mercury electrode.

In this connection therefore we decided to investigate the possibility of getting stable, clearly defined, and reproducible oscillographic polarograms on solid electrodes.

1. Depolarization of Solid Electrodes under Conditions Used for Oscillographic Polarography

The basic reason which, for a long time, has hindered introduction of solid electrodes into polarography, has been the phenomenon of their polarization caused by unsteadiness in the polarographic current with time, for a constant value of the applied potential. From a number of methods of eliminating this phenomenon, we chose one proposed by Skobets [4] electrochemical depolarization by short circuiting the electrodes. Its application to oscillographic polarography is discussed below.

The saw tooth voltage applied to the polarographic cell is in the form of separate triangular impulses (Fig. 1). In the interval between impulses the polarographic circuit remains closed to the output resistor of the impulse generator. If this resistance is chosen so that it is small compared with the internal resistance of the electrolyzer (of the order of 100 Ω), it may be reckoned that under these conditions, the polarographic cell will be short circuited; depolarization of the electrodes occurs. We call the ratio of the time during which the impulse is applied to the circuit, to the total time for a complete cycle (period duration), the coefficient of use of the period, and denote it by the letter β:

$$\beta = \frac{T_1}{T_2}.$$

It was found experimentally that a sufficient degree of depolarization, and renewal of the electrode surface is achieved for values of $\beta = 0.75$–0.85.

2. Description of the Oscillographic Polarograph

A type EO-4 oscillograph was used for our polarographic studies, in conjunction with a one-tube attachment (Fig. 2) which we constructed. The saw tooth voltage is applied from the deflecting plate of the oscillograph cathode ray tube through a divider C_1, R_1, R_2 to the grid of tube L_1. The tube is operated in the negative region of grid voltage, with partial shut-off of anode current (Fig. 3). Thanks to this, the continuous saw tooth voltage is converted into separate triangular impulses with the requisite value of β. Low tension is taken from the resistor R_4 and applied to the polarograph cell E. A resistor R_5 is connected in series with the electrolytic cell. The potential

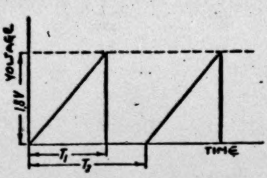


Fig. 1. Nature of the voltage applied to the electrolytic cell.

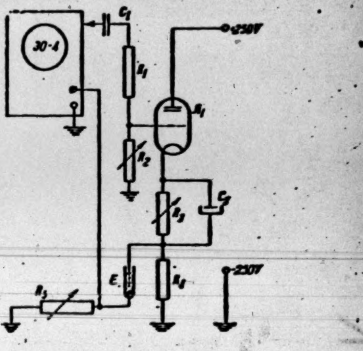


Fig. 2. Scheme of the polarographic attachment for the cathode ray oscillograph.

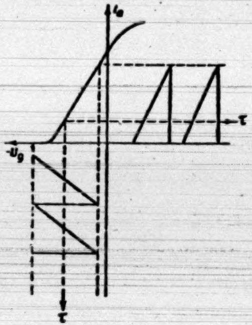


Fig. 3. Operating conditions for the tube in the oscillographic attachment.

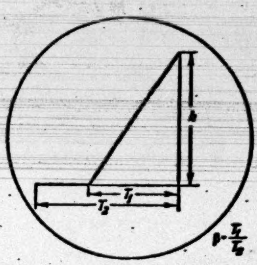


Fig. 4. Image obtained on regulating the apparatus.

drop across the resistor is proportional to the polarographic current. This voltage is applied to the vertical input of the oscillograph. The loop R_3C_2 is meant to provide a constant negative shift to the tube grid. To regulate the operating conditions of the tube and the amplitude of the voltage obtained, R_2, R_3, and R_5 are made variable resistors.

To standardize the apparatus a resistance box (type KMS-6 e.g.) is fitted into the circuit instead of the electrolytic cell. Impulse amplitude and β are then determined from the character and height of the image (Fig. 4).

By means of an oscillograph type EO-4 in conjunction with the attachment just described, oscillographic polarograms were obtained for materials at concentrations of $0.5 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$ M/liter.

At lower concentrations it was necessary to insert another cascade of wide band amplification between the resistor and the input of the oscillograph. In such cases it became necessary to screen both the polarographic cell and the amplifier from external interference.

In contrast to oscillographic polarographs described in the literature, the attachment which we have suggested is very simple, and can be made independently with the minimum expenditure of time and materials. An attachment of this type can be successfully used also for studying oscillographic polarograms on dropping mercury and streaming electrodes.

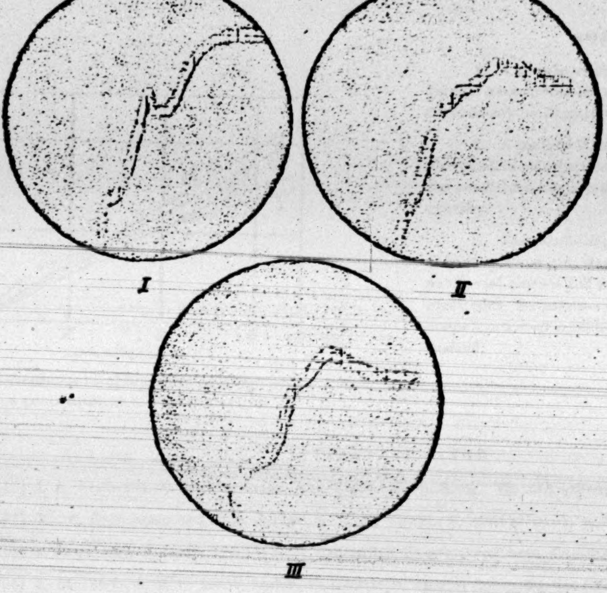


Fig. 5. Oscillographic polarograms: I) Copper and cadmium; II) bromine anion; III) iodine anion.

RESULTS

Oscillographic polarograms of the cations Cd^{2+} and Cu^{2+} in 1 N KCl, of the cation Pb^{2+} in 1 N KNO$_3$ and of the anions Br$^-$ and I$^-$ in 1 N KNO$_3$ were studied. The following electrodes were used: a micro electrode — a silver needle conical in shape, 3 mm long and with a diameter of ~0.3 mm at the base; a macro electrode — a silver plate, ~1 cm^2 in area. During oscillographic determinations of cations the micro electrode was the cathode, in the case of anions, the micro electrode was the anode. Both electrodes were amalgamated. Impulse frequency was 20 periods/second. $\beta = 0.75$.

The oscillograms for cadmium and lead were reminiscent in shape of the ordinary type of polarogram obtained by the visual method. The oscillogram for copper had a sharply defined maximum (Fig. 5,I). Br$^-$ and I$^-$ gave double and triple waves, reminiscent of normal polarographic waves(Fig. 5,II and III). Solution agitation affected wave height to some extent. The relation between wave height and concentration of the polarographed ion was linear in the case of Cd^{2+}, Cu^{2+} and Br$^-$ in solution, right up to concentrations of $1 \cdot 10^{-2}$ M/liter. In the case of Pb^{2+}, the relation was linear only up to a concentration of $5 \cdot 10^{-3}$ M/liter. The relation between I$^-$and concentrations was curve-linear (Fig. 6). All oscillograms were taken without preliminary removal of oxygen.

In contrast to the dropping mercury cathode, solid mocroelectrodes enable one to get stationary and very stable oscillograms. The height of the polarographic wave can be determined directly on a network superimposed on the oscillograph screen, so that there is no need to photograph images.

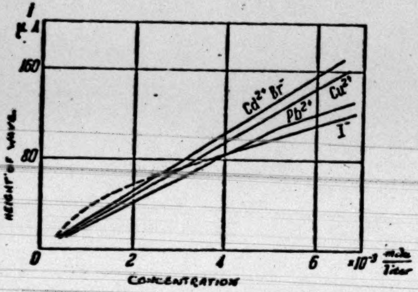


Fig. 6. Dependence of height of polarographic wave on concentration of ions in solution.

SUMMARY

1. A simple model of a one-tube polarographic attachment for use with an industrial cathode ray oscillograph has been constructed.

2. A method is suggested for the electrochemical depolarization of solid electrodes under the conditions employed in oscillographic polarography.

3. The possibility has been demonstrated of getting clear cut, stationary oscillograms for a number of cations and anions on solid amalgamated electrodes; the relation between wave height and concentration of reducible or oxidizable ions has been studied.

Received January 12, 1954

LITERATURE CITED

[1] L. A. Matheson, N. Nicols, Trans. Am.-Electrochem. Soc., 73, 193, (1938).

[2] Ya. P. Gokhshtein and N. A. Surkov, J. Anal. Chem., 8, 323 (1953) (T. p. 359)*.

[3] J. Heyrovsky, F. Sorm, and J. Foreit, Collection Czechoslov. Chem. Commun. 12, 11 (1947).

[4] E. M. Skobets, P. P. Turov, and V. D. Ryabokon, Factory Labs., 15, 414 (1949).

---

* T. p. = C. B. Translation pagination.

POLAROGRAPHIC DETERMINATION OF PLATINUM ON SOLID ELECTRODES. II

M. B. Bardin and Yu. S. Lyalikov

Kishinev State University

In some of the papers published on the polarography of platinum on the dropping mercury electrode, some authors have turned their attention to the nature of the wave obtained.

Thus, Heratimenko and Slendyk [1], have showed that in acid media, in the presence of platinum (and some of the other platinum group metals), a polarographic wave is obtained the height of which is approximately directly proportional to platinum concentration in solution. They established that this wave is a result of catalytic reduction of hydrogen, and is connected with a drop in its overvoltage on mercury.

Rius and Moler [2], during a polarographic study of the cyanide complex of quadrivalent platinum, established that the wave thus obtained is a result of reduction of quadrivalent platinum to the divalent state.

Laitinen and Onstott [3], investigated the possibility of adsorption and reduction of tetrachloroplatinite on the dropping mercury electrode.

We have been unable to find any published data on the mechanism of platinum reduction on solid electrodes.

Bearing in mind that platinum exists in two valency states, and, that in this connection, a complex ion is subjected to the polarographic process, it should be possible to advance a few interpretations of the reduction process which takes place on a platinum microelectrode.

It is known that if the free energies of the various oxidative states of a metal differ enough from each other, reduction will occur step-wise and that two waves will be obtained on a polarogram.

Having obtained two breaks on the current-voltage curve (Fig. 1) for solutions of chloroplatinic acid, one would expect, by analogy with the metals indicated, that platinum should give two diffusion zones on the polarogram, corresponding to its two valency states.

Nevertheless, taking into account the fact that the equilibrium potentials of the system $[PtCl_6]^{2-}/$ $/[PtCl_4]^{2-}$ and $[PtCl_4]^{2-}/Pt^0$ are very close to each other, respectively equal to + 0.72 V and + 0.73 V, one could postulate that the reduction of $[PtCl_6]^{2-}$ should only be accompanied by one polarographic wave. In this case, it would be necessary to account for the origin of the second wave and its nature.

The present article is devoted to solving these questions.

EXPERIMENTAL AND DISCUSSION OF RESULTS

The work was carried out on the polarographic set-up described previously [4].

Direct observation of the electrode surface showed that metallic platinum, in the form of platinum black, is already deposited within the potential range of the formation of the first wave. This fact indicated that during formation of the polarographic wave, the complex ion $[PtCl_6]^{2-}$, which is in solution, decomposes on the cathode, and that the final product is metallic platinum.

Nevertheless, it was still not clear whether or not the reduction proceeds step-wise through an intermediate stage of reduction to $[PtCl_4]^{2-}$ or proceeds straight through to metallic platinum.

To clarify the position, polarograms of divalent platinum solutions were taken.

Divalent platinum in the form of potassium chloroplatinite was prepared by reduction of potassium chloroplatinate with sulfurous acid [5].

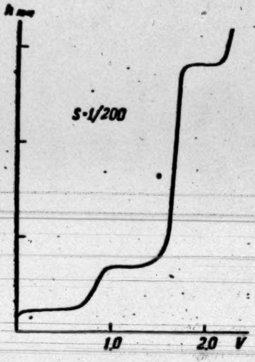


Fig. 1. Polarogram of a solution of H_2PtCl_6, containing 3.1 mg of platinum — volume 30 ml.

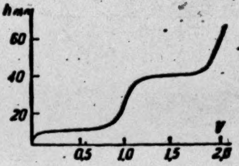


Fig. 2. Polarographic wave for divalent platinum in a solution of K_2PtCl_4.

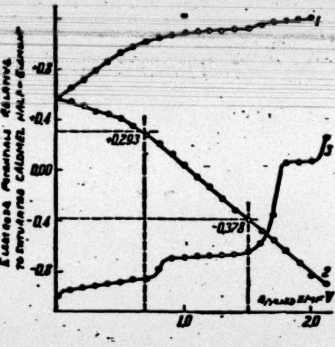


Fig. 3. Changes in electrode potentials when taking a polarogram:
1) Anode potential; 2) cathode potential; 3) polarogram of a solution containing 0.0018 g Pt in 25 ml.

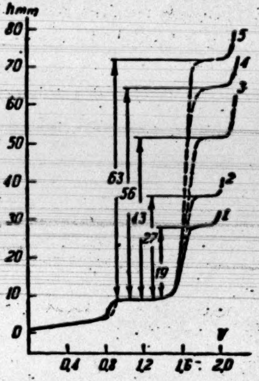


Fig. 4. Relation between wave height and acidity:
1) Polarogram of a H_2PtCl_6 solution;
2-5) addition of HCl. Total acid concentration in the electrolytic cell: 2) $1 \cdot 10^{-5}$ N;
3) $2 \cdot 10^{-5}$ N; 4) $3 \cdot 10^{-5}$ N; 5) $4 \cdot 10^{-5}$ N.

The crystals obtained were dried, an aliquot dissolved in water, and polarograms taken.

Fig. 2 illustrates the polarogram obtained for divalent platinum. As the figure shows, divalent platinum gives a clearly defined polarographic wave at the same potential as quadrivalent platinum.

This fact may serve as proof that the reduction process which occurs on the microcathode, and which determines development of the first wave on the polarogram (Fig. 1) is a reflection of the overall electrochemical reaction:

$$[PtCl_6]^{2-} + 2e \rightarrow [PtCl_4]^{2-} + 2Cl^-$$

$$\frac{[PtCl_4]^{2-} + 2e \rightarrow Pt^0 + 4Cl^-}{[PtCl_6]^{2-} + 4e \rightarrow Pt^0 + 6Cl^-}.$$

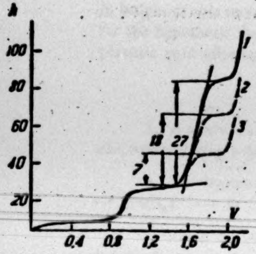


Fig. 5. Decrease in height of the second wave on addition of alkali: 1) Polarogram of H_2PtCl_6 solution; 2) 0.3 ml of 0.01 N NaOH added; 3) 0.6 ml of 0.01 N NaOH added.

On the basis of the results obtained above, it may be postulated that the second wave on the polarogram (Fig. 1) is not connected with platinum reduction, and that its character may be determined by some other reduction process.

To clear up the position, we determined electrode potentials during the time polarograms were taken. Potentials were determined with a type PPTV-1 potentiometer; a saturated calomel half element served as reference electrode. On Fig. 3 we give the curves for changes in cathode and anode potentials respectively, during polarography of chloroplatinic acid, the concentration of which, in terms of platinum was 0.0018 g in 25 ml.

It is evident from Fig. 3 that the potential at which the second wave starts lies within the limits −0.38-0.4 V relative to the saturated calomel electrode. This value is near the potential at which hydrogen is evolved, according to the value given by Kolthoff and Lingane [6], for a 0.001 N solution of hydrochloric acid on a platinized electrode. Bearing in mind that the work was carried out with chloroplatinic acid, it is quite possible that the second wave on the polarogram is determined by hydrogen reduction.

Results	First potential at which hydrogen is evolved relative to the saturated calomel electrode in V	Second potential at which hydrogen is evolved in V (satd. cal. elec.)	Applied voltage	
			At the first step on the curve	At the second step on the curve
According to Turov	−0.54	−1.0	1.94	2.4
Found by us	−0.38	−0.85	1.75	2.2

In order to verify this hypothesis we studied the effect of acidity on the character of the polarographic waves. One would expect that if the second wave belongs to hydrogen, its height should increase with increasing acidity. Chloroplatinic solutions were accordingly acidified with varying amounts of hydrochloric acid and polarograms taken. The acid was added from a microburet, and its normality calculated from the total volume of solution polarographed. Polarograms for platinum solutions containing varying amounts of hydrochloric acid are illustrated in Fig. 4. The increase in height of the second wave with increasing acid concentration may serve as an argument for the hypothesis that the second wave is a hydrogen reduction wave, while the platinum electrode is a sensitive indicator for the hydrogen ion. It should be noted that addition of alkali (Fig. 5), as one would expect, leads to a decrease in wave height.

The existence of two potentials for hydrogen evolution is in good agreement with experimental results of other authors who have studied this question.

Skobets and Kudra [7], established the existence of two hydrogen electrode potentials on a platinum cathode on the current — voltage curve in hydrochloric and sulfuric acid solutions. Krasilshchikov and coworkers [8], also established the existence of two hydrogen reduction potentials during cathodic polarization of acid solutions.

Turov [9], carried out a detailed study of the two potentials at which hydrogen is evolved.

The results which Turov gives for cathodic polarization in 0.005 N H_2SO_4 are very close to those which we got for the second wave.

The small differences may be explained by the fact that Turov worked on a smooth platinum electrode and at high concentrations, while, in our case, the cathode was always platinized to some extent because of the preliminary deposition of platinum on it; as a consequence, the potentials we found were shifted to more positive values.

The values of the electrode potential of the cathode during generation of the second wave, the increase in height of this wave with increasing acidity, and its decrease on addition of alkali, may serve as arguments for the hypothesis that the second wave obtained on the polarogram when polarograms are taken of chloroplatinic acid solutions, is a hydrogen reduction wave.

SUMMARY

1. A study has been made of the mechanism of the electrode process which occurs on platinum microelectrodes during polarographic investigation of aqueous solutions of chloroplatinic acid.

2. The hypothesis is advanced that the first wave is the result of an overall reduction process $[PtCl_6]^{2-} \rightarrow \rightarrow [PtCl_4]^{2-} \rightarrow Pt^0$, while the second wave is the result of hydrogen reduction $2[H_3O]^+ + 2e \rightarrow H_2 + 2H_2O$.

3. Since the second wave is a function of hydrogen ion concentration, then for analytical purposes one should use the first wave for platinum determination, because its height, as shown earlier [4], is proportional to platinum concentration.

Received July 10, 1954

LITERATURE CITED

[1] P. Herasimenko and J. Slendyk, Collection 5, 11,479 (1933).

[2] A. Rius and M. Molera, An. fis. quim., 45 (B), 1151 (1949).

[3] H. A. Laitinen and E. J. Onstott, J. Am. Chem. Soc., 72, 10, 4565 (1950).

[4] M. B. Bardin and Yu. S. Lyalikov, J. Anal. Chem., 10, 305 (1950).

[5] Inorganic Syntheses, Coll. II, 1951, p. 237.

[6] I. M. Kolthoff and J. Lingane, "Polarography", Moscow-Leningrad 1948, p. 416.

[7] E. M. Skobets and O. K. Kudra, J. Appl. Chem., 20, 11, 1176 (1947).

[8] A. I. Krasilshchikov, J. Phys. Chem., 18, 537 (1944); I. D. Nefedova and A. I. Krasilshchikov, J. Phys. Chem., 21, 7, 855 (1947).

[9] P. P. Turov, "Trans. Conference on Electrochemistry", Moscow, 1953, p. 86.

POLAROGRAPHIC INVESTIGATION OF THE CHLORIDE, BROMIDE, AND THIOCYANATE COMPLEXES OF CADMIUM IN ABSOLUTE ETHYL ALCOHOL

Ya. L. Turyan

Kishinev State University

It is a known fact that the solvent does not remain indifferent during complex formation, but has a substantial effect on the stability and composition of complex compounds. A study of this effect, particularly the effect of non-aqueous solvents on the instability constants of complex compounds, is of great importance, both for analytical chemistry, and for the theory of solutions.

Insufficient attention has been given to the instability constants of complex compounds in non-aqueous solutions. Markman and Turyan [1], by means of a polarographic study of the iodide complexes of cadmium in a mixed solvent ($H_2O + C_2H_5OH$), established that a considerable drop occurs in the instability constant of $[CdI_4]^{2-}$ on increasing the alcohol content. Thus, K_n in 65% C_2H_5OH was found to be ~ $1/10^4$ of the value of K_n in H_2O. The coordination number of the complex ion does not change during the process.

There is a very large amount of published material on the instability constants of complex compounds in aqueous solutions [2]. Particularly detailed studies have been made of the chloride, bromide, and thiocyanate complexes of cadmium, using various methods: polarography [3,4], potentiometery [5], and solubility [6]. This led us to study the stability of the same complexes in absolute ethyl alcohol. It should be noted that according to Yatsimirsky's classification [7], all the addenda indicated belong to the same class of covalent addenda. It is therefore of interest to make a comparative study of them in non-aqueous solvents, in compounds with the same central ion.

EXPERIMENTAL*

Solutions for polarographic work were prepared from analytical grade chemicals: $Cd(NO_3)_2$, NH_4NO_3, NH_4Cl, NH_4Br, NH_4CNS and $CaCl_2$ (after removal of water of crystallization). 6-10 cadmium concentrations in the range 0.1-0.9 mM/liter for each solution were tested to discover any proportionality between diffusion current and cadmium concentration in alcoholic solution, and to determine the resistance of the polarographic cell. The strength of NH_4NO_3, in the presence of which the polarographic character of the simple cadmium ion was investigated was 0.01 M. The concentration of complexing agent was varied within the following limits: NH_4Cl 0.01-0.09 M, NH_4Br 0.03-0.2 M, NH_4CNS 0.01-0.7 M and $CaCl_2$ 0.11-1.1 M. The alcohol was made absolute with CaO, and was subsequently treated with sodium metal; it had a strength of 99.8% (according to density measurements). Polarographic measurements were carried out on a hand-made visual set-up with a carefully checked rheocord, a shunt made from two decade resistance boxes, and a M-21 mirror galvanometer. The external reference electrode ($Hg/NH_4Cl_{\text{satd.}}$ in C_2H_5OH)** was isolated from test solution by an intermediate solution of 0.1 M NH_4NO_3 in C_2H_5OH. Electrical contact was established through two diaphragms of porous glass. The use of an intermediate solution proved essential for complete prevention of penetration of Br^- and CNS^- into the reference electrode, and of Cl^- ions into test solution. The potential of the reference electrode with respect to the null hydrogen electrode in C_2H_5OH was + 0.096 V. Oxygen was removed, by passing hydrogen saturated beforehand at the test temperature (25 ± 0.3°) with alcohol vapor through the test solutions. For the study of cadmium solutions with NH_4NO_3, NH_4Cl, NH_4CNS, and $CaCl_2$ respectively as supporting electrolytes, capillaries with the following characteristics were used $m^{2/3} t^{1/6} = 2.33$ mg$^{2/3}$ sec$^{1/2}$., and in the case of NH_4Br as supporting electrolyte, a capillary with the characteristics $m^{2/3} t^{1/6} = 1.78$ mg$^{2/3}$ sec$^{-1/2}$. m and t were measured at a potential of 0.6-0.7 V.

---

[*] E. I. Greenberg took part in the experimental work.

[**] All the potentials given below are relative to the reference electrode.

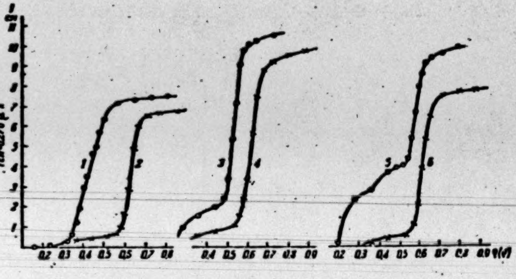


Fig. 1. Polarographic waves for cadmium (c= 0.384 mM/liter) in C_2H_5OH in the supporting electrolytes:
1) 0.01 M NH_4NO_2: 2) 0.09 M NH_4Br; 3) 0.09 M NH_4CNS; 4) 0.09 M NH_4Cl; 5) 0.5 M NH_4CNS; 6) 0.33 M $CaCl_2$.

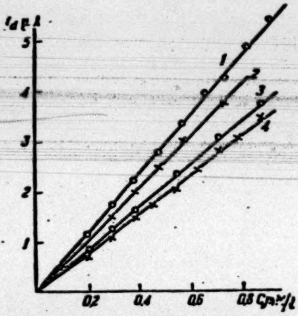


Fig. 2. Relation between diffusion current and cadmium concentration in C_2H_5OH. using the supporting electrolytes:
1) 0.09 M NH_4Cl; 2) 0.09 M NH_4CNS;
3) 0.09 M NH_4Br; 4) 0.55 M $CaCl_2$.

Clearly defined polarographic waves with no maxima were obtained for cadmium, for all the supporting electrolytes tested in C_2H_5OH solution(Fig.1), though nothing was added to the solution to suppress maxima. The half-wave potentials of cadmium in the presence of NH_4Cl, NH_4Br, NH_4CNS and $CaCl_2$ were considerably more negative than those obtained in solutions of 0.01 M NH_4NO_3 $(\varphi_{1/2})_s = -0.369$ V and $K_s = 5.11$ μ A/mM/l), where cadmium is present as simple ions. This indicates the formation, in alcoholic solution, of fairly stable chloride, bromide and thiocyanate cadmium complexes.

The diffusion currents were found to be proportional to cadmium concentration (Fig. 2). NH_4CNS at concentrations greater than 0.1 M proved to be an exception. In this case there was observed an appreciable increase in the diffusion current constant with increasing metal concentration. It should be noted that the cadmium waves in these solutions, in contrast to cadmium waves at concentrations of NH_4CNS less than 0.1 M, exhibited large residual currents, and, moreover, the principal wave was preceded by a poorly defined small wave (Fig. 1), which was not observed on polarograms with a pure background. In view of these complications determinations of the stability and composition of thiocyanate complexes were only carried out in solutions with concentrations of $NH_4CNS \leqslant 0.1$ M.

A necessary condition which allows use to be made of the polarographic method for determining the instability constant and the composition of complex particles, is the reversibility of the electrical reduction of the latter on a dropping mercury electrode. A careful check on this point is particularly important in the case of non-aqueous solutions whose polarographic behavior has been insufficiently studied; very little information is to be found in the literature on the nature of electrical reduction of metals from non-aqueous solutions.

In order to check on the reversibility of the process, we adopted the normal method [8], of verifying the validity of the theoretical equation for a polarographic wave:

$$\varphi = \varphi_{1/2} - \frac{0.0591}{n} \lg \frac{i}{i_d - i} \qquad (1)$$

TABLE 1

Polarographic Characteristics of Cd^{2+} in the Presence of NH_4Cl and $CaCl_2$

NH_4Cl							$CaCl_2$			
C_x mM/l	log C_xf_x	K_c μ A/mM/l	$\varphi_{1/2}$ in V	$\Delta\varphi_{1/2}$ in V	p	$K_n \cdot 10^{13}$	C mM/l	K_c μA/mM/l	$(\varphi_{1/2})_x$ in V	$\Delta\varphi_{1/2}$ in V
0.010	−2.217	6.11	−0.542	−0.173	3	3.70	0.110	5.59	−0.581	−0.212
0.027	−1.887	6.83	−0.570	−0.201	3	4.64	0.330	4.72	−0.618	−0.249
0.054	−1.668	5.70	−0.589	−0.220	3	4.05	0.550	3.83	−0.628	−0.259
0.072	−1.582	5.70	−0.599	−0.230	3	3.30	0.715	3.66	−0.637	−0.268
0.090	−1.520	5.83	−0.603	−0.234	3	3.78	0.935	3.20	−0.646	−0.277
					Mean	3.89	1.100	2.56	−0.650	−0.281

TABLE 2

Polarographic Characteristics of Cd^{2+} in the Presence of NH_4Br

C_x mM/l	log C_xf_x	K_c μA/mM/l	$(\varphi_{1/2})_k$ in V	$\Delta\varphi_{1/2}$ in V	p	$K_p \cdot 10^{13}$
0.03	−1.858	4.30	−0.577	−0.208	3	2.69
0.05	−1.693	4.22	−0.599	−0.230	3	1.45
0.07	−1.590	4.23	−0.610	−0.241	3	1.27
0.09	−1.519	4.23	−0.614	−0.245	3	1.53
0.20	−1.264	4.53	−0.632	−0.263	3	2.36
					Mean	1.86

TABLE 3

Polarographic Characteristic of Cd^{2+} in the Presence of NH_4CNS

C_x mM/l	log $C_x \cdot f_x$	K_c μ A/mM/l	$(\varphi_{1/2})_c$ in V	$\Delta\varphi_{1/2}$ in V	p	K_n 10^3
0.01	−2.217	6.10	−0.471	−0.102	2	1.57
0.03	−1.858	5.97	−0.502	−0.133	2	0.70
0.05	−1.693	5.87	−0.514	−0.145	2	0.58
0.09	−1.519	5.13	−0.520	−0.151	2	0.99
0.10	−1.485	5.35	−0.522	−0.153	2	0.99
					Mean	0.97

by constructing a graph of $\varphi - \log \frac{i}{i_d - i}$. The respective corrections for ohmic drop in voltage was applied to all points on the polarographic waves. For this, the resistance of the polarographic cell was determined by means of a method described by Stromberg and Bykov [9]. The results of the verification of Equation (1) are shown in Fig. 3. The tangent of the angle made by the straight lines $\varphi - \log i/i_d - i$, given in Fig. 3 (tg α), for all test solutions was near to the theoretical value of 0.030, which testifies to the reversibility of the reduction of the chloride, bromide, and thiocyanate complexes of cadmium in alcoholic solutions, and to the fact that 2 electrons ($n = 2$) participate in the electrode reaction.

Since the electrode reactions are reversible the following equations [8], can be used:

$$\frac{\Delta (\varphi_{1/2})_c}{\Delta \log C_x \cdot f_x} = -p\,\frac{0.0591}{n} \tag{2}$$

and

$$(\varphi_{1/2})_c - (\varphi_{1/2})_s = \Delta\varphi_{1/2} = \frac{0.0591}{n}\log K_n + \frac{0.0591}{n}\log\frac{f_c K_s}{f_s K_c} - p\,\frac{0.0591}{n}\log C_x f_x \tag{3}$$

for determining the coordination number of the complex particles p and the instability constant K_n.

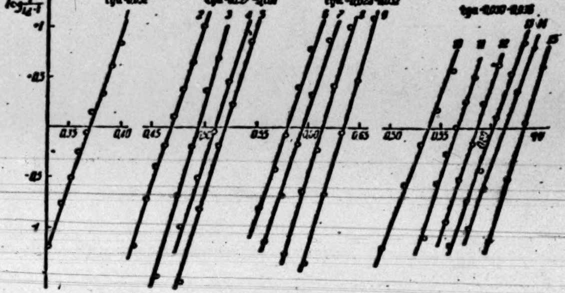


Fig. 3. The relation $\varphi - \log\frac{i}{i_{d-i}}$ (Cd concentration = 0.384 mM/liter):
1) 0.01 M NH_4NO_3; 2, 3, 4, 5) 0.01 M, 0.03 M, 0.05 M, 0.09 M NH_4CNS;
6, 7, 8, 9) 0.03 M, 0.05 M, 0.09 M, 0.2 M NH_4Br; 10, 11, 12, 13) 0.01 M,
0.027 M, 0.054 M, 0.09 M NH_4Cl; 14, 15) 0.33 M, 0.715 M $CaCl_2$.

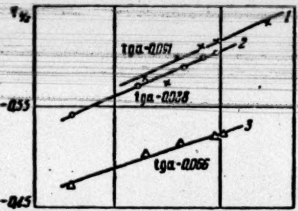


Fig. 4. Relation between the half-wave potential of cadmium and the logarithm of addenda activity:
1) NH_4Br; 2) NH_4Cl; 3) NH_4CNS.

TABLE 4

Instability Constants of the Chloride, Bromide, and Thiocyanate Complexes of Cadmium in H_2O and C_2H_5OH

Solvent	Complex composition		
	$[CdBr_3]^-$	$[CdCl_3]^-$	$Cd(CNS)_2$
H_2O	$3.98 \cdot 10^{-4}$	$2.00 \cdot 10^{-3}$	$1.05 \cdot 10^{-2}$
C_2H_5OH	$1.86 \cdot 10^{-13}$	$3.89 \cdot 10^{-13}$	$0.97 \cdot 10^{-8}$

A characteristic of the polarographic determination of p and K_n by means of Equations (2) and (3) in a non-aqueous solvent with a low dielectric constant is the inadmissibility of assuming $f_x = 1$, as is sometimes done for an aqueous solution. At the same time there is hardly any published information available on activity coefficients for salts in non-aqueous solvents. Taking into account the low concentration of the test complexing agents NH_4Cl, NH_4Br, and NH_4CNS (0.01-0.2 M), we assumed that the activity coefficients of these salts in C_2H_5OH are equal to the activity coefficients of HCl in C_2H_5OH at the same dilutions. The activity coefficients of HCl in C_2H_5OH were taken from "The Chemist's Handbook" [10].

For calculating K_n, logarithm f_c/f_s was neglected; the value of logarithm K_s/K_c was calculated numerically.

The half-wave potentials and the diffusion current constant, for each addendum concentration were determined from the means of 6-10 measurements, at various cadmium concentrations. These values; $(\varphi^1/_2)_c$ and K_c are given in Tables 1, 2, and 3 and the graphical relation between $(\varphi\, 1/_2)_c$ and log $C_x f_x$ – on Fig. 4. The linear relation established between $(\varphi 1/_2)_c$ and log $C_x f_x$ (Fig. 4) points to a stable composition for the chloride, bromide and thiocyanate complexes of cadmium in the addenda concentration range tested. From the slopes of the straight lines (Fig. 4) (tg α) the following compositions were established [by means of Equation (2)] for the complexes considered: $[CdCl_3]^-$, [CdBr and $Cd(CNS)_2$. From Korshun, Malyugin, and Balabanova's work [4], it follows that in aqueous solution, chloride and bro mide complexes of cadmium with the same composition are formed at considerably higher concentrations of addenda. Moreo on the basis of Vasilev and Proukhina's results [3], it may be postulated that in aqueous solutions of NH_4Cl and NH_4Br, in the salt concentration range 0.01-0.2 M, no complex formation occurs, in general. Thus, in alcohol, complex formation between Cd^{2+} ions and Cl^-, and Br^-, starts at addenda concentrations which are considerably lower than in similar aqueous solutions.

Results of calculations of the instability constants of the chloride, bromide, and thiocyanate complexes of cadmium in C_2H_5OH are given in Tables 1, 2, and 3. Instability constants were calculated as in Vasilev and Proukhina's work [3], for all addenda concentrations, after which the mean value of the constants was determined. For comparison, the respective instability constants in aqueous solutions, taken from the review article of Yatsimirsky [2], are adduced in Table 4.

It is clear from Table 4 that the stability of the complexes formed between cadmium and the halide addenda in alcohol changes in the same order as in aqueous solution: $Br^- > Cl^-$, though the differences in the instability constants in alcohol are somewhat less than in water. On the basis of Table 4 it is also possible to draw a conclusion re the significant increase in stability of the bromide, chloride, and thiocyanate cadmium complexes on switching over from aqueous solutions to solutions in absolute ethyl alcohol. Thus, the instability constant of the halide complexes decreases approximately 10^9 times. Changes in the instability constant with the nature of the solvent is related to changes in the electrostatic energy of ionic charge and discharge [11]. Hitherto, it has not been possible to evaluate this effect quantitatively for the test compounds. The only fact that clearly emerges is that on changing over to a solvent with a lower dielectric constant (alcohol), the change in the electrostatic free energy of the dissociation process of the test complexes, increases; consequently, this leads to a decrease in the instability constant of the complex.

In conclusion, let us examine the polarographic characteristics of cadmium in a supporting electrolyte of $CaCl_2$ in C_2H_5OH (Table 1). Unfortunately, we were unable to calculate K_n and p for these solutions, because no data was available on the activity of $CaCl_2$ in C_2H_5OH. The values for the activity of C_2H_5OH in solutions of $CaCl_2$ in C_2H_5OH published [12], do not permit even an approximate calculation of the activity of $CaCl_2$ at the dilution we want.

From a comparison of the polarographic characteristics of cadmium in supporting electrolytes of NH_4Cl and $CaCl_2$ respectively (Table 1), it follows that $\Delta\varphi_{1/2}$ (0.09 M NH_4Cl) is greater than $\Delta\varphi_{1/2}$ (0.11 M $CaCl_2$). This can hardly be explained by a decrease in activity of the addenda in 0.11 M $CaCl_2$. It is more probable that C_xf_x in 0.11 M $CaCl_2$ is greater than C_xf_x in 0.09 M NH_4Cl. From this it may be postulated that $\Delta\varphi_{1/2}$ (0.09 M NH_4Cl) is greater than $\Delta\varphi_{1/2}$ (0.11 M $CaCl_2$) as a result of an increase in the instability of the chloride complex of cadmium in the presence of the calcium cation. The effect of the cation of the outer sphere on complex stability has already been noted in the literature [3]. With increasing $CaCl_2$ concentration the shift in the half wave potential of cadmium to the negative side increases. When this happens the diffusion current constant, apparently, as a result of an increase in viscosity, drops appreciably.

SUMMARY

1. The polarographic behavior of the chloride ($Cd(NO_3)_2 + NH_4Cl$, $CaCl_2$), bromide ($Cd(NO_3)_2 + NH_4Br$) and thiocyanate ($Cd(NO_3)_2 + NH_4CNS$) complexes of cadmium has been investigated in absolute ethyl alcohol.

2. It has been shown that there is a proportionality between cadmium concentration in the presence of the complexing agents indicated, and diffusion current; electrical reduction from alcoholic solution has also been shown to be reversible.

3. The composition of the complexes formed has been determined: $[CdCl_3]^-$ (0.01-0.09 M NH_4Cl), $[CdBr_3]^-$ (0.03-0.2 M NH_4Br) and $Cd(CNS)_2$ (0.01-0.1 M NH_4CNS) as well as the instability constants $K_{[CdCl_3]^-} = 3.89 \cdot 10^{-13}$, $K_{[CdBr_3]^-} = 1.86 \cdot 10^{-13}$ and $K_{Cd(CNS)_2} = 0.97 \cdot 10^{-8}$. Instability constants in C_2H_5OH are considerably lower (for the Cl and Br complexes ~. 10^9 times less) than the instability constants of the same complexes in H_2O.

4. It has been shown that in C_2H_5OH, complex formation between Cd^{2+} ions and Cl^-, and Br^- starts at concentrations of NH_4Cl and NH_4Br which are appreciably less than in H_2O.

Received June 13, 1954

LITERATURE CITED

[1] A. L. Markman and Ya. I. Turyan, J. Gen. Chem., 22, 1926 (1952) (T. p. 1973)*.

[2] K. B. Yatsimirsky, Prog. Chem., 22, 410 (1953).

[3] A. M. Vasilev and V. I. Proukhina, J. Anal. Chem., 6, 218 (1951).

[4] I. A. Korshunov, N. I. Malyugina, and O. M. Balabanova, J. Gen. Chem., 21, 620 (1951) (T. p. 685)*.

[5] H. Riley, and V. Gallafent, J. Chem. Soc., 1, 514 (1932).

[6] I. M. Korenman, J. Gen. Chem., 18, 1233 (1948).

[7] K. B. Yatsimirsky, "Thermochemistry of Complex Compounds", USSR Acad. Sci. Press, 1951, p. 111.

[8] I. M. Kolthoff and J. J. Lingane, "Polarography", State Chem. Press, 1948, p. 169.

[9] A. G. Stromberg and I. E. Bykov, J. Gen. Chem., 19, 245 (1949) (T. p. 209)*.

[10] "The Chemist's Handbook", State Chem. Press II, 1952, p. 474.

[11] S. Glasstone, "Introduction to Electrochemistry", Foreign Lit. Press, 1951, p. 433.

[12] Landolt-Börnstein, Phys.-Chem. Tabl. Erg., Bd. III, 1936, p. 2159.

---

* T. p. = C. B. Translation pagination.

MICROSYNTHESIS AND IDENTIFICATION OF SOME MERCURIZED ARYLAMINES

I. M. Korenman and A. A. Belyakov

Scientific Research Institute for Labor Hygiene at Gorky

The synthesis of organo-mercury compounds has found application in analytical chemistry for the detection and determination of mercury salts [1, 2], ternary alcohols [3], aldehydes and ketones [4], and, more fully, double and ternary bonds [3, 5-9].

Aniline, methylaniline, ethylaniline, dimethylaniline, and diethylaniline are readily mercurized by mercuric acetate to form crystalline, fairly stable derivatives, mono-mercurized in the para position (aniline also gives an ortho compound) and dimercurized aniline according to the following scheme [10, 11]:

$$C_6H_5R + HgAc_2 \rightarrow RC_6H_4HgAc + HAc; \quad C_6H_5NH_2 + 2HgAc_2 \rightarrow H_2NC_6H_3(HgAc)_2 + 2HAc,$$

where

$$R = NH_2; \ -NHCH_3; \ -NHC_2H_5; \ -N(CH_3)_2; \ -N(C_2H_5)_2.$$

We managed to carry out such a synthesis with a drop (25-50 mm³) of the arylamine solution (microsynthesis) with the aim of identifying both the arylamines and their mercurized derivatives.

TABLE 1

Characteristics of Mercurized Arylamine Precipitates*

Precipitate	Crystal form of the colorless precipitate	Interference colors and extinction angle	Sensitivity of arylamine reaction in one drop in mg	Melting point in °C	
				Published data [10, 11]	Compound obtained by microsynthesis
1,4-Aminophenyl mercuriacetate	Prisms, parallelograms (Fig. 1)	Intense (yellow, red, and green), 42-44°	0.5	166-167	164-167
1-Amino phenyl 2,4-dimercuriacetate	Elliptical plates (Fig. 2)	Weak, 28-30°	0.25	206	202-206
1,4-Methylamino-phenylmercuriacetate	Leaves, irregular plates	Weak, 90°	1.0	149 (decomp.)	148-150 (decomp.)
1,4-Ethylamino-phenylmercuriacetate	Plates, needles and prisms	Intense (yellow, orange, green), 22-25°, a little at 14-16°	1.0	130	127-130
1,4-Dimethyl-aminophenyl-mercuriacetate	Needles and prisms (Fig. 3)	Needles — weak prisms — intense (yellow, red, green) 21-23°, 14-16°	0.1	163	163-165
1,4-Diethyl-aminophenylmer-curiacetate	Fine needles and clusters	Weak, 90°	0.5	104.4 (decomp.)	103-105 (decomp.)

---

* All microphotographs were taken at a magnification of 100.

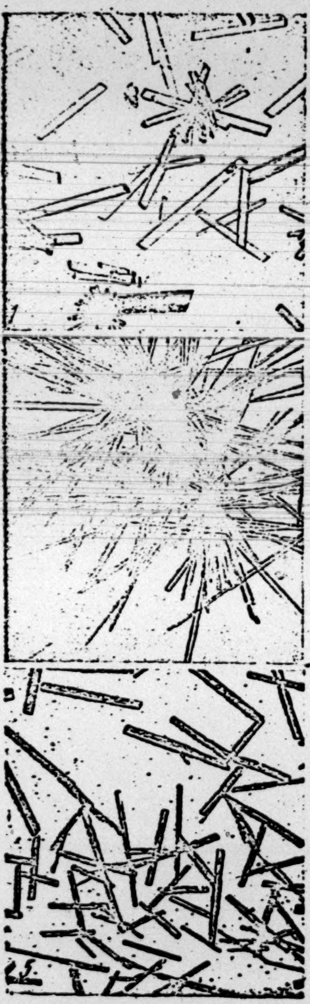


Fig. 1. 1,4-Aminophenylmercuriacetate.

Fig. 2. 1-Aminophenyl-2,4-dimercuriacetate.

Fig. 3. 1,4-Dimethylaminophenylmercuriacetate.

Fig. 4. 1,4- Aminophenylmercurichloride.

Fig. 5. 1 4-Diethylaminophenylmercuriacetate.

TABLE 2

Characteristics of Precipitates Which Are Formed During Reactions Between Mercurized Arylamines and Certain Anions

Compound	Reagent	Crystal form of the colorless precipitate	Interference colors and extinction angle of crystals	Limit of identification in γ in 2 mm^3	Maximum crystal size in μ
1,4-Aminophenylmercuriacetate					
Aqueous solution	NaCl	Rosettes of fine petals	Weak, oblique extinction	0.3	150
Acetic acid solution	$Na_2S_2O_3$	Plates	Weak, 32-35°	1.4	1000
1,4-Methylaminophenylmercuriacetate					
Aqueous solution	NaCl	Fine plates, thick needles	Intense (yellow, blue) 6-7°	0.15	250
1,4-Ethylaminophenylmercuriacetate	$Na_2C_4H_4O_4$	Plates	Weak, 27-30°	2.0	220
1,4-Dimethylaminophenylmercuriacetate Acetic acid solution	KCN	Rosettes, plates	Intense (yellow, red, green), 35-37°	0.25	350
1,4-Diethylaminophenylmercuriacetate Aqueous or acetic acid solution	KCN	Rods, plates	Intense (yellow, blue), 90°	0.25	200
Acetic acid solution	$Na_2S_2O_3$	X-shaped crystals, prisms, changing over into cigar-shaped crystals	Intense (yellow, orange) 17-20°, 30-32°, 90°	3.0	150
Acetic acid solution	NaCl	Rods and bunches of rods (Fig. 5)	Intense (yellow, red, green), 90°	1.5	350
1-Aminophenyl-2,4-dimercuriacetate Acetic acid solution	NaCl	Clusters of fine needles	Weak, oblique extinction	0.2	120

Existing methods of identifying arylamines, based, e.g. on differences in colors of the azo dyes prepared from them, or in their reaction products with lignin or bindone [12-15], are hardly applicable to the group of compounds under discussion, because such reactions are not specific enough.

We identify the organo-mercury compounds obtained by micro-synthesis by means of microcrystalloscopic reactions with the salts of various acids.

Microsynthesis can be carried out either directly from the arylamine itself, in which case it is necessary to add 20-40 mm^3 of a saturated aqueous solution of mercuric acetate, or a solution of the same salt in 50% ethyl alcohol to 10 mm^3 of amine; or, from a drop of the aqueous or alcoholic solution of the amine. When the second technique is adopted it is necessary to use dilute solutions of mercuric acetate. We used 5-10 mm^3 of the reaction mixture for identifying the arylamine and its mercuric derivative; the rest, 40-45 mm^3 can be used for preparing the pure compound for determining its melting point.

To carry out the microsynthesis we prepared solutions of 1 g of mercuric acetate $Hg(CH_3COO)_2$ in 5 ml of water or in 10 ml 50% ethyl alcohol, containing 3-4 drops of 25% acetic acid. The solutions were filtered after preparation.

When working with alcoholic or aqueous solutions of aniline, the primary solutions of mercuric acetate are diluted 2-5 times with water or 50% alcohol. To a drop (25 mm^3) of an aqueous or alcoholic solution of mercuric acetate in a small tube is added an equal volume of an alcoholic or aqueous solution of aniline. The amorphous precipitate which often forms in dilute solutions disappears on subsequent heating, particularly on shaking. When studying dilute aniline solutions, the mixture is heated to the boil (repeated heating is sometimes necessary) and on cooling the whole is stirred with a glass rod to initiate crystallization. 2-3 mm^3, often already containing a precipitate, is placed on an object glass, and after a few minutes the precipitate of the mono- or dimercurized compound examined under the microscope (Figs. 1 and 2).

Formation, during microsynthesis of a mixture of mono- and dimercurized or of only dimercurized aniline indicates use of excess mercuric acetate. In order to prepare the monomercurized aniline, for identification of which we have suggested several microcrystalloscopic reactions, it is essential to use more dilute mercuric acetate solutions. Synthesis is successful for a content of not less than 0.25 mg aniline in 25 mm^3 solution.

The characteristics of mercurized arylamine precipitates are given in Table 1.

We have only included some of the microphotographs and tables characterizing the microreactions.

The crystalline precipitate which separates out on the object glass is washed 2-3 times with 10 mm^3 lots of water, a piece of filter paper is then dipped in the edge of the drop + precipitate to remove the liquid. The washed precipitate is dissolved on gentle heating and is mixed by means of a glass rod with 5-7 mm^3 of water or 7-10% acetic acid; a drop of solution is combined with a crystal or drop of reagent. The reagents used are the sodium and potassium salts of various acids. The characteristic crystalline precipitate which is formed is examined microscopically (Table 2). The remainder of the solution in the tube is then transferred with a pipet to an object glass, washed slightly, and after precipitation of most of the crystals, the mother liquor is removed with filter paper. The precipitate is washed as described above with 2 drops of water and a drop of 96% alcohol; it is then dried for 30-45 minutes at 30-40° and its melting point determined (Table 1). The amount of mercurized aniline required for melting point determination is obtained from not less than 1 mg aniline in 25 mm^3 of primary solution.

In contrast to aniline, microsynthesis with aniline derivatives is carried out in alcoholic solutions of the arylamines (in 96% alcohol) and mercuric acetate (in 50% alcohol) at room temperature. The order in which the various operations of synthesis, purification, and identification of the mercurized compounds is carried out, is the same as that described above for aniline (Table 2).

10-15 minutes after the mercuric acetate solution has been mixed with the solution of secondary or tertiary arylamines, the mixture is transferred by means of a pipet to an object glass, the solution allowed to evaporate and the precipitate collected. In order to determine the melting point of the mercurized compounds, it is necessary to have an amount of product equal to 1 mg of methyl- or ethylaniline, 0.2 mg of dimethylaniline, and 0.5 mg of diethylaniline respectively in 25 mm^3 of solution (Table 1). For the rest, the procedure is identical to that described for microsynthesis with aniline.

Other characteristic reactions, apart from those indicated in Table 2 can be used for the identification of test organo-mercury compounds; e.g. reactions with nitrates or nitrites, p-aminosalicylic acid, or cyanides [16-18].

The difference in shape between crystals of mercurized compounds and their reaction products with certain anions, the melting points, and also certain crystalloscopic constants, all together, permit the presence of an arylamine in solution to be readily established.

Synthesis and identification of a mercurized arylamine takes 20-30 minutes (excluding melting point determination).

SUMMARY

1. The possibility has been demonstrated of microsynthesizing organo-mercury derivatives of some arylamines for analytical purposes. The technique for carrying out a micro synthesis with one drop (50 mm^3) of solution is described. The sensitivity is 0.1-1 mg of arylamine in a drop.

2. Microcrystalloscopic reactions for identifying some mercurized arylamines have been suggested. The limit of identification is 0.15-3 γ of the organo-mercury compound in 2-3 mm^3 of solution.

Received May 5, 1954

LITERATURE CITED

[1] V. I. Kuznetsov, "Trans. All-Union Conf. on Anal. Chem., Moscow-Leningrad, 1939, p. 1, 86; Factory Labs., 11, 656, 768 (1945).

[2] A. A. Medvedovsky, Ukrainian Chem. J., 1, 36 (1951).

[3] G. Meyer, "Analysis and Determination of the Structure of Organic Materials", Kharkov-Kiev, 1938, p. 283, 691.

[4] R. Shreiner and R. Fyuson, "Systematic Qualitative Analysis of Organic Compounds, Moscow, 1950.

[5] M. N. Marushkin and A. P. Belenkaya, J. Anal. Chem., 5, 358 (1950).

[6] "Analytical Methods for Organic Compounds", Symposium edited by A. P. Terentev, Moscow, 1951, p. 96.

[7] R. Pyke, A. Kahn and D. Roy, J. Anal. Chem. 19, 65 (1947).

[8] T. Connor and G. F. Wright, J. Am. Chem. Soc., 68, 256 (1946).

[9] I. I. Strizhevsky, Factory Labs., 14, 24 (1948); I. I. Strizhevsky and A. S. Zaitsev, Factory Labs., 17, 1311 (1951).

[10] L. G. Makarova and A. N. Nesmeyanov, "Synthetical Methods for Organo-mercury Compounds" Moscow-Leningrad 1945, p. 43.

[11] F. Whitmore, "Organic Mercury Compounds", Leningrad, 1938, p. 188.

[12] L. M. Kulberg and Z. V. Ivanova, J. Anal. Chem., 2, 198 (1947).

[13] S. N. Burmistrov, J. Anal. Chem., 1, 265 (1946); 5, 39 (1950).

[14] G. Ya. Vanag, J. Anal. Chem., 5, 110 (1950).

[15] A. F. Plate, Trans. Commission on Anal. Chem., Moscow-Leningrad, 1947, p. 153.

[16] I. M. Korenman and A. A. Belyakov, J. Anal. Chem., 7, 52 (1952) (T. p. 55)*.

[17] I. M. Korenman and A. A. Belyakov, "The Medicinal Industry of the USSR" 6, 35 (1951).

[18] I. M. Korenman and A. A. Belyakov, J. Anal. Chem., 8, 168 (1953) (T. p. 185)*.

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

COLORED ADSORPTION REACTIONS OF MAGNESIUM HYDROXIDE

V. I. Kuznetsov

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences, Moscow

INTRODUCTION

Colored adsorption reactions may be considered as belonging to the category of "colored solid phase reactions", i.e. colored reactions of a type where the color which is characteristics of the reactions is connected with the presence of a solid phase. If, for any reason, the solid phase dissolved, then the color which is a result of the reaction, disappears[1].

Solid phase colored reactions differ from many other categories of colored reactions, in that it is not always possible to explain the color formed as the result of a reaction, on the basis of characteristic features of the molecular structure of the reaction product, or to assign formulas to them which can account for the color developed. This is quite understandable. The color of a solid material depends not only on its molecular structure, but also on crystal structure, which determines the crystallo-optical properties of the solid phase, or on other characteristics of the structure of the solid phase. These latter characteristics are not reflected in modern structural formulas for either organic or inorganic compounds; accordingly, molecular structural formulas which are often capable of giving a satisfactory explanation of the characteristics of the color of a material in a dissolved state, cannot give an explanation of the characteristics of the color of a material, which are often observed, when the materials are present in the form of a solid phase [1].

Magnesium hydroxide possesses a very strongly developed capacity to change the color of organic materials sorbed by it, as well as a strongly developed absorptive capacity [2]. When alkali is added to a solution of a magnesium salt containing some colored organic material, the magnesium hydroxide that is precipitated very often sorbs the colored compound and changes its color. The color of the magnesium hydroxide suspension formed often differs to a lesser or greater degree from the color of the alkaline solution of organic material used. Sometimes, a very distinct difference in color is observed, e.g. the alkaline solution may be yellow, while the color of the magnesium hydroxide suspension is red (titan yellow).

The hydroxides of some other elements are also capable of changing the color of organic materials sorbed by them, but, compared with magnesium hydroxides, the hydroxides of other elements, with the partial exception of cadmium and nickel, can only change the color to a completely insignificant extent. For this reason, color reactions for magnesium, which depend on the unique capacity of its hydroxide just discussed, have good contrast and selectivity, together with a fair sensitivity. A few gamma of magnesium per ml gives a clear cut reaction.

Many color reactions for magnesium have been described in the literature, which are based on the capacity of magnesium hydroxide when formed to adsorb colored organic reagents and change their color. E.g. colored reactions with the following reagents have been described: titan yellow [26], and its analogs; colorimetric determination of magnesium — to which many articles have been devoted; various other azo compounds [6-9, 15, 21, 29]; diazoamino compounds [20, 22]; triazines [10, 13, 30]; hydroxyanthraquinones [4, 15]; naphthazarine [19]; and amine oxidation products of unknown structure [7], and any others.

It is quite obvious that unless any individual reactivity of the reagents is expressed, reactions with all these reagents have the same main advantages and disadvantages. Selectivity of action will also be the same. All those factors which complicate precipitation of magnesium as the hydroxide interfere with all these reagents to a similar extent. However, the factors which affect the absorptive capacity of magnesium hydroxide, affect the absorption reaction to a different extent, because of the unequal capacities of the various reagents to be sorbed.

The difference in sensitivity to magnesium of reactions of this type described in the literature, can be explained by differences in individual evaluation of the sensitivity by different research workers, and particularly by variations in appearance of the precipitates, which is determined by the contrast of the reactions and by the extent of adsorption of a given dye.

We want to emphasize this point in connection with the fact that from time to time there appear in periodical literature descriptions of "new" highly sensitive color reactions for magnesium, based on the mechanism under discussion [12, 13, 29, 30].

Search for new color reactions of this type for magnesium presents no difficulties, since practically any dye used industrially which is soluble in alkali, and very many other colored materials, give color reactions for magnesium. Some colorless compounds which form colored oxidation products in the reaction mixture under the action of oxygen or under the influence of some other mechanism, are also suitable. Such are the reactions with p-phenylenediamine [7, 27], diphenylcarbazone [23], and hypoiodide + iodide [28].

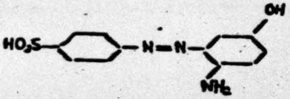
The color reactions under discussion lead to the formation of so called "adsorbed compounds". The amount of reagent adsorbed, and the color intensity related to this, follow the adsorption laws. The reagent and magnesium hydroxide do not form, in the usual sense of the term, a reaction product with a definite composition [14, 17]. There are indications that e.g. no differences can be detected between magnesium hydroxide and its reaction product with titan yellow by x-ray or electron microscope methods [24]. Accordingly, we are of the opinion that the information which crops up in the literature about the supposed formation of compounds with a definite chemical composition during these reactions [3, 4] — sometimes even formulas are advanced for these alleged compounds — needs to be backed by more solid evidence.

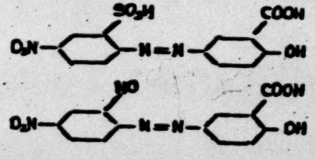
The Relation Between Reagent Structure and Capacity to Give Color Reactions

By comparing the formulas of colored compounds which give bright color reactions with magnesium hydroxide, with the formulas of those which do not, some research workers have determined the characteristic atomic groups, whose presence in a reagent molecule is connected with the capacity of the reagent to give colored adsorption reactions with magnesium hydroxide [5, 8, 9, 11, 20].

It has been pointed out e.g. that in the case of hydroxynitroazo compounds it is essential that the groups $-NO_2$ and $-OH$ should be in the ortho or para position (not in the meta position) with respect to the azo group [5, 8, 9] etc.

Such conclusions based on generalization of experimental results on many compounds, have, in many cases, received actual confirmation. It is possible however, to give examples where such generalizations are not enough. Thus, 3-hydroxy-5-aminoazobenzene-4'-sulfonic acid despite the fact that the hydroxyl group is meta with respect to the azo group, instead of the required ortho or para positions, gives a bright color reaction with magnesium. Alkaline solutions of this material which are rose colored, form violet precipitates in the presence of magnesium. Mention can also be made of azo compounds containing NO_2 and OH groups in the ortho or para positions with respect to the azo group, which, nevertheless, do not give color reactions with magnesium. The following are examples of such compounds and a number of other azo substituted salicylic acids. The reason for the absence of a color reaction in this case, is the too stable coupling of the magnesium by the salicylate group of the azo group, as compared with the stability of the adsorbed compound of the nitrohydroxyazo compound with magnesium hydroxide. No color reactions for magnesium with nitrohydroxyazo compounds are obtained either when salicylic acid itself is added.





A more cautious approach would be to consider that the colored adsorption reactions of magnesium hydroxide, in a general way, are not only dependent on the presence in the molecule of a colored reagent of some definite atomic groups, at least, in the form accepted at present in theories on organic analytical reagents. Magnesium hydroxide reactions are solid phase reactions, and first consideration should be given to the hitherto unexplained structural characteristics of the "adsorbed compound" of the colored solid phase. The molecular structure of the reagent plays a subsidiary role, and only in cases of possibly identical structures for the colored solid phase is the impression created that reaction results are determined by the molecular structure of the colored compound.

Colored compounds which give color reactions with magnesium hydroxide have a variety of structures. Apart from the nitrohydroxyazo compounds just indicated, many other azo compounds not containing the nitro group give color reactions e.g. titan yellow [26], azo blue, stilbene orange R, etc. [21]. Color reactions are also given by indophenols containing either nitro or amino groups [Table 1], and ones not containing hydroxy groups, as well as diazoamino compounds [20, 22]; several hydroxyanthraquinones, e.g. quinalizarin [25] which contains no nitrogen at all. Finally, an inorganic reagent which contains sodium iodide and hypoiodite NaIO + NaI, give a similar reaction with magnesium. The pale yellow iodine solution which is obtained by addition of NaOH, forms a brown precipitate with magnesium [28].

If one tried to include the molecular structures of all these compounds under the hypothesis re characteristic atomic groups, one would have to assume the existence of too many characteristic groups.

The color changes of the reagent during adsorption on the surface of magnesium hydroxide may be connected with polarization phenomena. Under the influence of a strong field the solid surface of the reagent, apart from the structural characteristics of the solid phase, may itself undergo some changes. It is not clear however, what is the scope of these changes, assuming that the reagent changes into another form which has a different structure, as has been assumed in several instances in the literature [6, 8, 19].

It is not clear either whether these explanations extend to reagents in which it is difficult to visualize a change in molecular structure of the reagent to another colored form with a different structure.

In conclusion we have adduced a short table of new colored adsorption reactions of magnesium hydroxide with reagents of varying structures (Table 1).

Reagents for the Colorimetric Determination of Magnesium

As a consequence of good selectivity, contrast, and sensitivity, colored adsorption reactions of magnesium hydroxide are of interest as a basis for the development of colorimetric methods of determining magnesium. Particularly well known is the method with titan yellow, to the analytical application of which for magnesium determination a vast amount of work has been devoted [16, 18, 31]. A reagent which is suitable for colorimetric determination of magnesium, should give reproducible, stable colors, which do not change for small sodium hydroxide concentration changes.

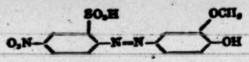
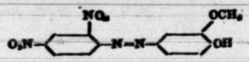
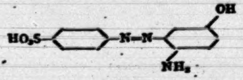
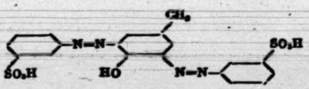
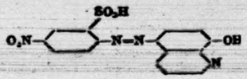
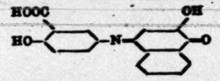
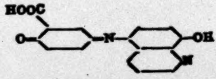
The changeability of colors with time is connected with aging of magnesium hydroxide.

On aging, the capacity of magnesium hydroxide to adsorb reagents decreases. If magnesium hydroxide precipitate which has adsorbed a reagent is allowed to stay in contact with the solution from which it was formed, then, according to the length of time for which it is allowed to stand, part of the initially adsorbed reagent will go back into solution again. Increasing the NaOH concentration in solution has a similar effect on the precipitate formed; it washes off the adsorbed reagent. In both cases the original color of the precipitate changes, the precipitate becomes pale, and may, in certain cases, even be completely decolorized.. The time it takes for a precipitate to change its color appreciably, differs from reagent to reagent; it takes a long time in the case of titan yellow which is used for the colorimetric determination of magnesium and a short time for the reagent magneson 1 (2,4-dihydroxy-4'-nitro-azobenzene), which complicates the use of this reagent for quantitative magnesium determination. If the magnesium hydroxide precipitate is aged long enough, a decreased adsorption capacity is observed even in the case of titan yellow. Shraibman [17], notes that the reagent should be added before the sodium hydroxide, since magnesium hydroxide precipitated beforehand, particularly after long standing, adsorbs titan yellow to a considerably less extent than at the moment of formation.

It is possible that in the case of reagents of similar structure, there is a simple relation between the size of the colored reagent molecule and its capacity to be adsorbed on magnesium hydroxide. Colored reagents with large molecules which form colloidal solutions are readily adsorbed. The loss by magnesium hydroxide of the capacity to adsorb reagents as a result of aging is not so marked in the case of reagents with high molecular weights, as it is for

TABLE 1

Colored Adsorption Reactions of Magnesium Hydroxide

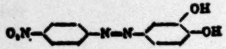
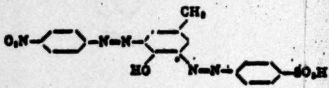
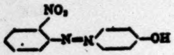
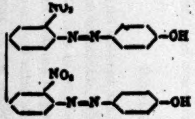
Experiment number	Reagent	Color in alkaline media	
		Reagent solution	Magnesium hydroxide suspension in the presence of reagent
1		Rose	Blue-violet
2		Violet-red	Blue
3		Rose	Violet
4		Red-violet	Blue
5		Violet	Blue
6	Congo-red	Red-orange	Raspberry-red
7		Orange	Red-violet
8		Rose-orange	Violet
9	Oxidation products of p-aminophenyl in alkali solution by air (22)	Red-brown	Dark-blue

reagents with low molecular weights. It is possible to choose reagents, which, having been adsorbed by magnesium hydroxide at the moment when the latter is formed, within a few minutes are completely desorbed back into solution. Reagents of this type should prove of interest for studying aging of precipitates. Examples of such reagents are given in Table 2 together with comparisons which illustrate the effect of reagent molecular weight on desorption. A particularly significant example of this effect is given by a comparison of reagents Numbers 3 and 4, the molecule of the latter apparently being a double version of Number 3.

It can be assumed that new reagents for colorimetric determination of magnesium should be sought among colored reagents with not too great a molecular weight. There exists, in all probability, some optimum molecular size, since when the size of the colored molecule is too large, changes in its ionic state affect the color to a relatively small extent. Accordingly, in such cases, the contrast of the colored reaction may not be high enough.

In trying to get good contrast for color reactions with new reagents, it should be borne in mind that after adsorption of the colored reagent on magnesium hydroxide, the light absorption curve is shifted towards the long wave side of the spectrum. One should therefore select reagents, whose alkaline solutions absorb on the very edge of the visible short wave side of the spectrum, i.e. in the violet, or even with a maximum in the ultraviolet. In other works for visual determination it is especially desirable that the alkaline solutions of the reagents should be yellow or orange.

TABLE 2

Experiment number	Reagent	Molecular weight	Color in Alkaline Medium		
			Reagent solution	Suspension of Magnesium Hydroxide+ Reagent	
				At the moment of formation	After the time indicated
1	2	3	4	5	6
1		259	Blue	Blue-green	After a few seconds blue
1a	Ditto on addition of $Pb(NO_3)_2$	259	Ditto	Ditto	Becomes blue slower than 1
2		427	Violet	Green	Blue after a few seconds, blue violet after 3 mins, violet after.
2a	Ditto on addition of $Pb(NO_3)_2$	427	Ditto	Ditto	Green after a few seconds, blue after 4 minutes
3		229	Yellow	Orange	Yellow after 1-2 minutes
3a	Ditto on addition of $Pb(NO_3)_2$	229	Ditto	Ditto	Orange after a few minutes
4		456	Orange-red	Violet	Violet after 1 hour

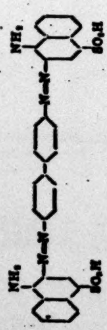
(Table continued on next page)

TABLE 2 (continued

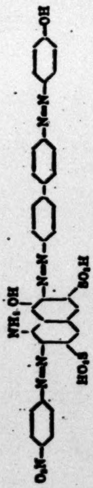
1	2	3	4	5	6
4a	Ditto on addition of $Pb(NO_3)_2$	456	Ditto	Ditto	Ditto
5	Congo red*	652	Red-orange	Raspberry red	Raspberry after 1 hour
6	Direct-green**	754	Dirty-green	Grey-blue	Grey-blue after 1 hour

---

*



**



Stability of Magnesium Hydroxide

Colors

It is possible to stabilize the colors of magnesium hydroxide caused by colored reagents, even those colors given by reagents with low molecular weights, by using stabilizers whose action can be conveniently compared with that of protective colloids. Lead hydroxide gives good protection.

When lead compounds are used two methods can be adopted, either the use of alkali containing lead as plumbite, or addition of a soluble lead salt to the magnesium salt solution follows by introduction of reagent and then addition of alkali. Even small amounts of lead give good protection. When lead is used, it is possible to get colors which are stable with time and to alkali, even with a reagent which has such a simple structure as, e.g. magneson 1(3,4-dihydroxy-4'-nitroazobenzene). The efficiency of lead as a stabilizer is clearly demonstrated by comparing the results given in Table 2. Moreover, when lead hydroxide is used, the suspensions formed are more stable and sediment less readily.

The use of a protective agent such as lead hydroxide increases the number of reagents which are suitable for the colorimetric determination of magnesium. At the same time, the effect of other factors becomes less marked. A practical procedure for carrying out a colorimetric determination of magnesium on the basis of the variant will be described elsewhere.

SUMMARY

Known colored adsorption reactions of magnesium hydroxide, which are carried out by precipitation of magnesium hydroxide in the presence of colored reagents, belong to the category of so called solid phase reactions. The color change of the reagent adsorbed by magnesium hydroxide is connected with the structure of the solid phase; it is difficult to tie it up with the structure of the reagent molecule.

The capacity of magnesium hydroxide to adsorb a dye decreases on aging. In some cases, colored reagents adsorbed by freshly precipitated magnesium hydroxide, may revert into solution if the precipitate is allowed to stay in contact with the solution. Reagents with high molecular weights are more strongly adsorbed, and are held

more firmly than reagents of a similar structure but with a low molecular weight. Coprecipitation of magnesium hydroxide with lead hydroxide inhibits desorption of reagent from magnesium hydroxide.

Received January 8, 1954

LITERATURE CITED

[1] V. I. Kuznetsov, Prog. Chem., 18, 75 (1949).

[2] J. W. McBain, and R. C. Dunn, J. Colloid Sci., 3, 303 (1948).

[3] N. I. Blok, "Qualitative Chemical Analysis", State Chem. Press, 1952, p. 165.

[4] S. A. Voznesensky, "Inner Molecular Compounds and Their Significance for Analytical Chemistry", State Gen. Sci. Tech. Press 1938, pp. 102-109.

[5] L. M. Kulberg, J. Anal. Chem., 3, 45, (1948).

[6] L. M. Kulberg, J. Gen. Chem., 8, 1132 (1938).

[7] L. M. Kulberg, J. Gen. Chem., 17, 39 (1947).

[8] L. M. Kulberg, J. Gen. Chem., 22, 969 (1952) (T. p. 1023)*.

[9] L. M. Kulberg and Z. V. Ivanova, J. Gen. Chem., 17, 601 (1947).

[10] G. T. Mikhalchishin, Ukrainian Chem. J., 19, 332 (1953).

[11] V. Ya. Pochinok, M. S. Marenets, and E. D. Smaznaya-Ilina, Ukrainian Chem. J., 19, 2, (1953).

[12] Kh. N. Pochinok and A. P. Marchenko, Ukrainian Chem. J., 17, 417 (1951).

[13] Kh. N. Pochinok and V. Ya. Pochinok, J. Anal. Chem., 4, 244 (1949); 6, 288 (1951).

[14] F. Feigl, "Spot Analysis" Gen. Sci. Tech. Press, 1937, p. 313; F. Feigl, Chemistry of Specific, Selective and Sensitive Reactions, N. Y., 1949, p. 547.

[15] F. Feigl, "Spot Analysis", Gen. Sci. Tech. Press, Moscow 1937, p. 317.

[16] E. B. Sandell, "Colorimetric Determination of Trace Amounts of Metals", State Chem. Press, 1949, p. 290.

[17] S. S. Shraibman, Factory Labs., 13, 930 (1947).

[18] E. Abrahamczik, Mikrochemie ver. Mikrochem. Acta., 33, 209 (1948).

[19] J. V. Dubsky and E. Wagner, Microchemie, 17, 186 (1935); 22, 108 (1937).

[20] F. P. Dwyer, Austral. Chem. Inst. J. Proc., 5, 32, 67, 149 (1938).

[21] E. Eigriwe, Z. anal. Chem., 76, 354 (1929).

[22] E. Eigriwe, Z. anal. Chem., 118, 98 (1938).

[23] F. Feigl, Z. anal. Chem., 72, 113 (1927).

[24] O. Glemser and W. Dautzenberg, Z. anal. Chem., 136, 254 (1952).

[25] F. L. Kahn, H. Wolf and G. Jäger, Ber., 57B, 1394 (1924).

[26] I. M. Kolthoff, Chem. Weekbl., 24, 254 (1927).

[27] L. La Rosa, Ann. chim. appl., 22, 725 (1932).

[28] W. I. Petraschenj, Z. anal. Chem., 71, 291 (1927).

[29] H. Rath and A. Sanchez, According to Chemical Abstracts, 40, 4885 (1946).

[30] L. Sacconi, Gazz. chim. ital., 78, 219 (1948).

[31] C. Urbach and E. Baril, Mikrochemie, 14 (N. F. 8) 343 (1934).

---

* T. p. = C. B. Translation pagination.

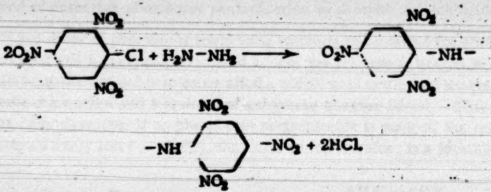
BLANK
PAGE

ANALYTICAL APPLICATION OF THE FORMATION OF HEXANITROHYDRAZOBENZENE

A. I. Cherkasov and L. M. Kulberg[*]

The N. G. Chernyshevsky Saratov University

Symmetrical hexanitrohydrazobenzene is formed under certain conditions as a result of interaction between trinitrochlorobenzene (picryl chloride) and hydrazine, according to the scheme [1]:



Acid salts of hexanitrohydrazobenzene with ammonium and the alkali metal ions have a red color in solution, sometimes a violet color. On this basis we have suggested previously, methods for the detection and quantitative determination of traces of hydrazine and potassium [2, 3].

Further study of the formation of hexanitrohydrazobenzene has shown that using this reaction as a basis, it is possible to work out methods for detecting several organic and inorganic compounds.

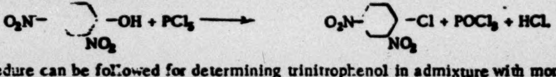
a) Detection of Trinitrochlorobenzene in the Presence of Mono- and Dinitrochlorobenzene

The chemistry of the reaction is expressed by the equations given above; the analytical technique employed is as follows. On a filter paper are successively placed a drop of a 1% aqueous solution of hydrazine sulfate, a drop of a 5% aqueous solution of sodium hydroxide and a drop of an acetone solution of trinitrochlorobenzene; a rose color develops. If no trinitrochlorobenzene is present, no color develops. It is possible, in this way, to detect 3. 10^{-8} g of trinitrochlorobenzene at a limiting dilution of 1:430,000.

The presence of comparatively large amounts of the mono- and dinitrochlorobenzenes as well as the trichloro compound, does not interfere with the reaction. Thus, for a ratio of trinitrochlorobenzene to mono- and dinitrochlorobenzene (or their mixtures) of 1:1,000, i.e. when only 0.1% of the trinitrochlorobenzene is present, it is easy to carry out the reaction. If no trinitrochlorobenzene is present, the color which develops is determined purely by the presence of the mono- and dinitrochlorobenzenes, viz. a weak yellow color.

b) Detection of Trinitrophenol in the Presence of Mono- and Dinitrophenols

From what has been said above, it is clear that mono- and dinitrochlorobenzenes do not react with hydrazine sulfate to form products which are rose or red in color. This fact served as a basis for developing a new method of detecting trinitrophenol (picric acid) in the presence of mono- and dinitrophenols. To carry out this reaction, it is necessary to convert trinitrophenol into trinitrochlorobenzene (picryl chloride); usually this is carried out by heating picric acid (trinitrophenol) with phosphorus pentachloride [4]:



The following procedure can be followed for determining trinitrophenol in admixture with mono- and dinitrophenols: a small amount of material to be tested for trinitrophenol is taken in a conical micro test tube, and a small grain of phosphorus pentachloride added; the two are mixed and heated in a burner flame to fusion. It is also necessary to heat the wall of the containing tube on which the slightly foaming mass rises. 3-5 drops of anhydrous acetone are added to the cooled mass and the whole mixed. By means of a capillary, a drop of the solution thus obtained is transferred to a filter paper, this is followed by a drop of a 1% aqueous solution of hydrazine sulfate, and the paper held over a flask containing concentrated ammonia solution. A red color develops. Under the same conditions, but in the absence of trinitrophenol, only a yellow color develops. When large amounts of trinitrophenol was present, the color may be a blue-violet. The reaction is reliable for a content of not less than 1% of trinitrophenol in the mixture.

---

[*] Deceased.

c) Detection of Phosphorus Pentachloride in the Presence of Phosphorus Trichloride

It was established in preliminary experiments that under the conditions which we used above, phosphorus trichloride does not react with picric acid to give trinitrochlorobenzene. This fact may be used for developing a method of detecting phosphorus pentachloride in phosphorus trichloride.

3-4 drops of phosphorus trichloride which is to be tested for phosphorus pentachloride are placed in a conical micro tube and a grain of picric acid added; the mixture is heated in a burner to the boil. During heating, the tube should be shaken in order to bring all the picric acid settled on the vessel walls into the reaction. The contents of the tube are cooled and 3-4 drops of anhydrous acetone added. This solution is then tested as before (b). A rose-violet color develops; if no phosphorus pentachloride is present, the color is yellow. When the phosphorus pentachloride is comparatively low (~ 0.1%), the color which develops is a brownish red.

SUMMARY

New qualitative reactions have been suggested for: trinitrochlorobenzene (picryl chloride) in the presence of mono- and dinitrochlorobenzene; for trinitrophenol (picric acid) in the presence of mono- and dinitrophenols; and for phosphorus pentachloride in the presence of phosphorus trichloride.

Received February 20, 1954

LITERATURE CITED

[1] H. Leemann and E. Grandmougin, Ber., 41, 1295 (1908).

[2] L. M. Kulberg and A. I. Cherkesov, J. Anal. Chem., 6, 384 (1951).

[3] A. I. Cherkesov, Thesis, Saratov, 1952.

[4] H. Jackson, and Gazzola, J. Am. 23, 384 (1842).

A COLOR TEST FOR THE PRESENCE OF LINOLENIC ACID GLYCERIDES IN OILS, AND A COLOR REACTION FOR CERTAIN ORGANIC COMPOUNDS WITH PICRIC ACID

T. A. Pkheidze and V. P. Goguadze

Tbilisi Scientific Research Chemico-Pharmaceutical Institute

In our previous article [1], it was shown that picric acid is capable of giving complex compounds with a representative of the aliphatic series — eleostearic acid. In this connection, it may be assumed that the method we suggested as a test for tung oil may be a group test for a number of oils containing not less than 1% of a compound with three or more conjugated bonds.

During our investigation we became interested in the question of to what extent is picric acid capable of giving colored interaction products with other representatives of the aliphatic series, and also whether the interaction of picric acid with pinene is the sole exception, or whether such a reaction with picric acid can be observed also with other representatives of non-aromatic and non-amminated compounds.

During a study of the reaction of picric acid with vegetable oils, in acetic acid media or in neutral solvents, it was shown that a number of oils such as linseed, plum, and soya bean oil, as well as fish oil, i.e. oils in which one would expect to find linolenic acid glycerides, show a tendency to develop a red color, not at room temperature, as happens in the case of tests for tung oil, but only after boiling the reaction mixture.

Nevertheless, in the case of vegetable oils, in which one would not expect to find linolenic acid glycerides, e.g. sunflower, cotton seed, and sesame oils, even after boiling, the reaction mixture showed no tendency at all to color development.

This last fact led us to suppose that the conditions which we have worked out, viz. interaction of picric acid with oils on boiling and acetic acid solution of picric acid, could be used as the basis of a new color test for detecting the presence of linolenic acid glycerides in oils. We suggest that this method is applicable in those cases where the test material is free from aromatic hydrocarbons which give color reactions with picric acid, even as mineral oils, and also in cases where amines, phenols, and oils of the type of tung oil, which contain conjugated bonds, etc, capable of giving a color reaction, are absent.

On the other hand, being interested in the study of the formation of colored derivatives of picric acid during its interaction with various organic compounds, we studied the reactions between an acetic acid solution of picric acid and a few representatives of certain classes of organic compounds including: hydrocarbons, alcohols, aldehydes, ketones, carboxylic acids, carbohydrates, glucosides, terpenes, vitamins, steroids and carotinoids.

It was shown experimentally that when the reaction mixture is heated, picric acid gives a color reaction with such aliphatic compounds as geraniol and tetrabutenediol, with compounds of non-aromatic character such as limonene, ionone, methylionone, and finally, with materials which are also non-aromatic in character but contain conjugated double bonds, such as ergosterol and carotinoids.

It was also shown experimentally that the sensitivity of these color reactions does not exceed the sensitivity of the color reaction of picric acid with eleostearic acid (91 mg/2ml), consequently, until a suitable intensifier has been found, these reactions cannot be used as a basis for developing a quantitative colorimetric method of determining these materials. When these compounds are present in test material in amounts less than one percent, the color tests can only be used for developing suitable qualitative tests.

Carotinoids proved to be an exception. Since, as far as we knew, sunflower oil does not give a color reaction with picric acid, we used solutions of carotinoids in sunflower oil as our test material. During interaction of an oil solution of carotinoids with an acetic acid solution of picric acid, or with a solution of picric acid in neutral organic solvents, instead of the red color which is usually observed in other cases, an intense green color is developed which is characteristic of carotinoids. The sensitivity of the reaction amounted to $1 \cdot 10^{-3}$ mg/ml and does not change in the course of 9 hours.

Carotinoids are known to give color reactions with many materials [2-4], including phenols and acetic acid [3, 5]. Nevertheless, all these reactions have the same drawback, viz. that although they are fairly sensitive, they are not stable. In addition, in the case of the color reaction of carotinoids with acetic acid its sensitivity is also low [3, 5].

In so far as acetic acid itself can give a weak color reaction with carotinoids, it might be thought that acetic and picric acids in conjunction might act as mutual intensifiers. Nevertheless, the use of this reaction for quantitative colorimetric determination of carotinoids is complicated by the color of picric acid itself.

Experiments on interactions between picric acid and other polyene materials containing double bonds continue.

Experimental Procedure for Carrying out the Reactions

2.0 ml of glacial acetic acid saturated at room temperature with picric acid was placed in a test tube and 15 drops of test material added. When the test material was solid, ~ 0.2 g was added.

After shaking, the test tube was heated in the flame of an alcohol burner and the contents boiled for 3-5 minutes.

Reaction Selectivity

Under the conditions just described, the following oils containing linolenic acid glycerides gave a red color: soya, linseed, mustard, and plum oils respectively and fish fat. A similar color was observed during tests on geraniol, tetrabutenediol, limonene, ergosterol, ionone, and methylionone. Carotinoids gave a green color.

The sensitivity of the method for all these compounds, apart from carotinoids, was 0.1 g / 2 ml.

Under the conditions described above, even after standing for 12 hours, no color changes were observed on testing the following oils which do not contain linolenic acid glycerides: sunflower, cotton seed, apricot, peach, tea seed, sesame, "kuragi", plum seed, cacao, castor, and almond oils respectively; no color reactions were given by the aliphatic chloro compounds: chloroform, dichloroethane, and ethyl iodide; the alcohols: methyl, ethyl, butyl, heptyl, hexyl, octyl, benzyl, phenylethyl, and phenylpropyl alcohols; the aldehydes: formaldehyde, butyraldehyde, benzaldehyde, and salicylaldehyde; the ketones: acetone, methyl ethyl ketone, benzophenone, and diacetone alcohol; the carbohydrates: glucose, saccharose, maltose, mannitol, lactose, and starch; the glucosides: total glucosides from digitalis, and saponin from tea seed; the acids: formic, acetic, propionic, caprylic, palmitic, stearic, oleic, tartaric, citric, benzoic, acetylsalicylic, salicylic, salol and nicotinic acid; the hydrocarbons, benzene and xylene; and cholesterol.

Sensitivity of the Reaction between Carotinoids and Picric Acid

10 ml of a mixture of dichloroethane and glacial acetic acid in the volume ratio of 1:1 (boiling point of mixture 90°), saturated with picric acid was taken. The mixture was placed in a test tube and 0.125 ml of a 1:1 by volume mixture of dichloroethane and acetic acid added; in each ml of mixture added was dissolved 0.015484 g of sunflower oil containing 0.5% (0.07742 mg) of carotinoids. On addition of not less than 0.125 ml of this mixture and subsequent heating of the test tube on a water bath followed by cooling to room temperature, a green color was observed. On this basis it follows that the lower sensitivity limit of the reaction, under the given conditions, is $1 \cdot 10^{-3}$ mg/ml. The upper limit was similarily found to be 0.1 mg/ml.

SUMMARY

A color test has been developed for detecting linolenic acid glycerides in oils. It has been found that an acetic acid solution of picric acid on heating with test material gives a color reaction with geraniol and tetrabutenediol, ionone, methylionone, ergosterol, and carotinoids.

Received August 28, 1953

LITERATURE CITED

[1] V. P. Goguadze and T. A. Pkheidze, J. Anal. Chem., 9, 308 (1954) (T. p. 341)*.

[2] V. N. Bukin, "Vitamins", Food Ind. Press, 1941.

[3] B. G. Savinov, "Carotin", Kiev, 1948.

[4] P. Karrer, and E. Jucker, Karotinoide, Basel, 1948.

[5] N. Deleano and J. Dick, Biochem. Z. 259 (1953).

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

THE CHROMATOGRAPHIC METHOD IN QUALITATIVE ANALYSIS

III. ANALYSIS OF As^{3+}, Sb^{3+}, and Sn^{2+}

K. M. Olshanova and K. V. Chmutov

Institute of Physical Chemistry, Academy of Sciences, USSR, Moscow

In our first article [1], we gave adsorption series for cations of the fifth analytical group (As^{3+}, Sb^{3+}, and Sn^{2+}) on various adsorbents. The present article contains details of a proposed method for qualitative chromatographic analysis of these cations on chromatographic aluminum oxide and Suifunite.

The adsorption series of the cations indicated is arranged on the adsorbents in the following order (Table 1).

TABLE 1

Adsorbent	Color of Adsorbent	Adsorption Series
Chromatographic aluminum oxide	White	As^{3+} > Sb^{3+} > Sn^{2+}
Permutite	White	reacts chemically with the solution of the cations
Bentonite-Askangel	White with a gray tinge	Ditto
Suifunite Nos. 55, 124, 127	Light yellow	As^{3+} > Sb^{3+} > Sn^{2+}

As^{3+}, Sb^{3+}, and Sn^{2+} cannot be detected on the adsorbent without development. Freshly prepared solutions of hydrogen sulfide and gaseous hydrogen sulfide were used as developers.

Chromatograms of As^{3+}, Sb^{3+}, and Sn^{2+} Developed with a Solution of Hydrogen Sulfide

A 0.25 N solution of the mixed cations was passed through chromatographic aluminum oxide. The column was washed with a solution of tartaric acid in order to avoid hydrolysis of the salts of tin and antimony, after which it was developed with a saturated solution of hydrogen sulfide. Chromatograms were thereby formed: on top, a light yellow zone of arsenic sulfide, followed by an orange zone of antimony sulfide, and below, a brown zone of tin sulfide; this confirms the adsorption series for fifth group cations established already.

On passing a similar solution of these cations through Suifunite with subsequent development, the same type of chromatogram with clearly defined zones was formed. Thus, Suifunite is completely suitable for detecting Group V cations. Development takes up to 60 minutes.

Using the method described, experiments were carried out with solutions of mixed Group V cations of different concentrations on alumina and Suifunite.

Results are given in Table 2.

TABLE 2

Normality of solution	Appearance of the chromatograms after development with a solution of hydrogen sulfide
0.3	Light yellow zone of As^{3+}, orange zone of Sb^{3+}, brown zone of Sn^{2+}. All the zones are clearly defined.
0.1	Zones are the same as above but less bright; the light yellow zone of As^{3+} is especially weak.
0.01	A grey Sn^{2+} was visible, no other zones could be distinguished.

The most clearly defined chromatograms were formed when a 0.3 N solution of cations was used.

All the cations can be clearly detected, but much time is spent in developing them. Consequently, the method was modified and gaseous hydrogen sulfide was used as a developer instead of a saturated solution of hydrogen sulfide.

Chromatographic Qualitative Analysis of Group V Cations

5 drops of a solution of a mixture of As^{3+}, Sb^{3+}, and Sn^{2+} was passed through an alumina column 4 cm high, and 0.6-0.7 cm in diameter. The chromatograms were washed with 5 drops of a concentrated solution of hydrochloric acid and developed with gaseous hydrogen sulfide. In the course of 1 minute the following chromatogram was formed: on top — a bright yellow zone of arsenic sulfide, followed by an orange zone of antimony sulfide, and below — a brown zone of tin sulfide. Similar results were obtained on a Sulfunite column.

In order to determine the sensitivity of this method when gaseous hydrogen sulfide is used as a developer, experiments were carried out with solutions of varying concentrations on chromatographic alumina.

Results are given in Table 3.

TABLE 3

Normality of solution	Appearance of chromatograms after development with gaseous hydrogen sulfide
0.17	Yellow As^{3+} zone, bright orange Sb^{3+} zone, dark brown Sn^{2+} zone. The boundary between the As^{3+} and Sb^{3+} zones was not clearly defined. Overall zone width 4.5 cm.
0.08	Ditto, but in comparison with the previous test, the zones were brighter and the boundary between As^{3+} and Sb^{3+} zones was more clearly defined. Total zone width 4 cm.
0.04	Orange zone of Sb^{3+}, brown zone of Sn^{2+}. No As^{3+} zone formed. Total width of zone 3.5 cm.
0.02	Bright orange zone of Sb^{3+}, brown ring of Sn^{2+}. Total zone width 2.5 cm.
0.01 to 0.002	Bright orange Sb^{3+} zone; narrow bright brown Sn^{2+} ring (traces).
0.001 to 0.00012	Orange Sb^{3+} zone, band width 0.8 cm.
0.00006-0.000007	Bright yellow Sb^{3+} zone, band width 0.5 cm.
0.000003	Column remains colorless.

The results given in Table 3 show that the best zones are obtained at concentrations of 0.08 to 0.17 N. Sn^{2+} ions can be detected at a minimum concentration in solution of $\sim$0.002 N, while antimony ions can be detected down to 0.000007 N. Accordingly the technique involving the use of hydrogen sulfide gas as a developer seems to be the most sensitive. The fact that with decreasing ion concentration in solution there is a corresponding decrease in zone width, is an important one, from the point of view that it should be possible to transform the method from a qualitative into a quantitative chromatographic method of analysis.

In order to get a more accurate picture of the state of affairs, additional experiments on the chromatography of Group V cations were carried out with various numbers of drops of solution at one and the same concentration. Analysis was carried out under the same conditions. Results are given in Table 4.

Table 4 shows that clearly defined zones are obtained in all cases, but the color is more intense, the higher the concentration. The height of the zone was again found to be related to ionic concentration in solution; this confirms the results of experiments given in Table 3.

Comparative Characteristics of Qualitative Methods for Detecting Group V Cations in Solution

In order to make a comparison of the characteristics of various qualitative methods for detecting Group V cations, test solutions were analyzed by three methods; 1) a macro method [3]; 2) a semi-micro method [4]; and 3) a chromatographic method. Results are given in Table 5.

Table 5 shows that the chromatographic method of detecting Group V cations has advantages over the other methods. Analysis takes 2-3 minutes, including preparation of an alumina column; further, no reagents, apart from concentrated hydrochloric acid and gaseous hydrogen sulfide, are needed, and only a small amount of these

TABLE 4

Number of drops of solution of mixed cations As^{3+}, Sb^{3+}, and Sn^{2+} taken for analysis	Total width of color of the chromatogram in cm	Appearance of chromatogram developed with hydrogen sulfide gas (from top to bottom)
	Analysis of 0.17 N solution of Group V cations	
5	4.5	Light yellow zone of As^{3+}, orange Sb^{3+} zone, and brown Sn^{2+} zone. In all cases the color intensity is the same; the best chromatogram was formed in the last case when 1 drop of test solution was used.
4	4.0	
	Analysis of 0.08 N solution of Group V cations	
5	4.0	Light yellow As^{3+} zone, orange Sb^{3+} zone, and brown Sn^{2+} zone.
4	3.5	
3	3.0	The zone colors were not so bright as in the previous case, but the zone boundaries were more clearly defined
2	2.8	
1	2.0	
	Analysis of 0.04 N solution of Group V cations	
5	3.5	No boundary between the light yellow As^{3+} zone and the orange Sb^{3+} zone. A brown Sn^{2+} zone was formed below.
4	3.0	
3	2.8	
2	2.0	The chromatogram was less clearly defined than in previous experiments
1	1.8	
	Analysis of 0.02 N solution of group V cations	
5	2.5	Light orange Sb^{3+} zone, below — brown Sn^{2+} ring.
4	2.3	
3	2.0	
2	1.8	
1	1.5	

TABLE 5

Comparison of Qualitative Methods of Detecting Group V Cations in Solution

Method	Normality	Test solution taken for analysis in ml	Time taken for an analysis in minutes
Macro method	0.2	50	180
″	0.2	10	85
″	0.2	5	52
″	0.2	2	45 Sb^{3+} and Sn^{2+} detected poorly.
″	0.2	1	As^{3+} readily detected, Sb^{3+} and Sn^{2+} scarcely detectable,
Semi-micro method	0.2	1	70
″	0.2	1	60
″	0.2	1	58
″	0.2	1	58
″	0.2	1	58
Chromatographic method	0.2	0.15	3
″	0.2	0.15	3
″	0.2	0.15	2
″	0.2	0.15	2.5
″	0.2	0.15	2
″	1.0	0.15	2
″	1.0	0.15	3
″	1.0	0.15	2
″	1.0	0.15	2
″	1.0	0.15	3

are required — 5 drops of concentrated hydrochloric acid per analysis. Analysis by other techniques require a fair amount of reagents and some apparatus.

SUMMARY

1. A qualitative chromatographic method has been developed for analysis of As^{3+}, Sb^{3+}, and Sn^{2+} when these are present simultaneously in solution.

2. The sensitivity of the method for detecting Group V cations using hydrogen sulfide in solution and as the gas respectively has been evaluated.

3. Macro. semi-micro, and chromatographic qualitative analytical methods for Group V cations have been compared. The chromatographic method is more rapid, requires less reagents, and is more sensitive than the other methods.

Received March 23, 1954

LITERATURE CITED

[1] K. M. Oleshanova and K. V. Chmutov, J. Anal. Chem., 8, 211, (1953) (T. p. 235)*.

[2] K. M. Oleshanova and K. V. Chmutov, J. Anal. Chem., 9, 2, 67 (1954) (T. p. 77)*.

[3] V. N. Alekseev, "Qualitative Analysis", State Chem. Press, 1951.

[4] I. P. Alimarin and V. N. Arkhangelskaya, "Qualitative Semi-Micro Analysis", State Chem. Press, 1952.

---

* T. p. = C. B. Translation pagination.

ACCURACY OF THE ION-EXCHANGE METHOD OF STANDARDIZING ALKALI

Yu. G. Titova

Institute of Food Chemistry, Krasnodar

In recent years ion-exchange chromatography has found increasing application in chemical analysis because this technique leads to a considerable saving of time without any loss of accuracy, as compared with classical analytical methods. A considerable number of articles by Lure and coworkers [1], has been devoted to separation of ions in a column containing an ion-exchange resin with subsequent quantitative determination of a series of cations and anions. Orlova [2], has described determination of free-acid in salt solutions.

The aim of the work described here was to determine the accuracy of the ion-exchange method for standardizing alkali by means of various salts. Oxalic acid $H_2C_2O_4 \cdot 2H_2O$ which is usually used for standardizing alkali possesses certain disadvantages, viz.: it is difficult to prepare in a pure state completely free from other salts and also containing exactly 2 moles of water of crystallization [3]. The salts of oxalic acid $Na_2C_2O_4$, $(NH_4)_2C_2O_4 \cdot H_2O$ are more stable and can be readily obtained in a pure state. We first of all studied the accuracy of alkali standardization by means of sodium and ammonium oxalate, and afterwards by means of other salts such as NaCl, $(NH_4)_2SO_4$, and $CuSO_4 \cdot 5H_2O$.

Fedorova [4], used an ion-exchange reaction on acid sulfo-coal for standardizing alkali by means of NaCl and $BaCl_2 \cdot 2H_2O$, and got satisfactory results. Since synthetic resins have practically completely replaced inorganic ion-exchange materials and sulfo-coal for the application of ion-exchange chromatography to chemical analysis in recent years [5], we used the cation-exchange resin SBS as the most suitable resin for analytical determinations.

TABLE 1

Standardization of Na_2CO_3-free NaOH Using Phenolphthalein as Indicator

Starting material	Normality of NaOH	Mean value of normality	Deviation from the mean in %	Mean deviation of individual determinations in %	Mean deviation of results in %	Normality
			By direct titration with $H_2C_2O_4$ solution			
$H_2C_2O_4 \cdot 2H_2O$	0.002083	0.002082	0.04	± 0.07	0.07 : $\sqrt{5}$ = 0.03	0.002082 ± ± 0.000001
Ditto	0.002083		0.04			
"	0.002078		0.19			
"	0.002083		0.04			
"	0.002083		0.04			
			Titration of acids formed by ion-exchange			
$Na_2C_4O_4$	0.002083	0.002079	0.19	± 0.18	0.18 : $\sqrt{10}$ = 0.05	0.002079 ± ± 0.000001
Ditto	0.002083		0.19			
$(NH_4)_2C_2O_4 \cdot H_2O$	0.002078		0.05			
Ditto	0.002082		0.09			
$(NH_4)_2SO_4$	0.002076		0.14			
Ditto	0.002076		0.14			
NaCl	0.002073		0.29			
Ditto	0.002073		0.29			
$CuSO_4 \cdot 5H_2O$	0.002084		0.24			
Ditto	0.002077		0.19			

TABLE 2

Standardization of NaOH Using Methyl Orange as Indicator

Starting material	Normality of NaOH	Mean value of normality	Deviation from the mean in %	Mean deviation of individual determination: in %	Mean deviation of results in %	Normality
By direct titration with HCl 0.05 N						
Fixonal HCl	0.002388	0.002386	0.08	± 0.10	$0.10 : \sqrt{5} = 0.05$	0.002386 ± 0.000001
Ditto	0.002381		0.20			
"	0.002388		0.08			
"	0.002384		0.08			
"	0.002388		0.08			
Titration of acids formed by ion-exchange						
Fixonal NaCl	0.002388	0.002389	0.04	± 0.17	$0.17 : \sqrt{10} = 0.05$	0.002389 ± 0.000001
Ditto	0.002381		0.34			
"	0.002381		0.34			
$(NH_4)_2SO_4$	0.002394		0.20			
Ditto	0.002388		0.04			
"	0.002395		0.25			
$CuSO_4 \cdot 5H_2O$	0.002394		0.20			
Ditto	0.002391		0.08			
"	0.002391		0.08			
"	0.002386		0.12			

Solutions (~0.05 N) of the test salts to be used were prepared by weighing out the respective amounts of chemically pure salts and dissolving them in the requisite amounts of water in standard flasks. An aliquot of such a solution – 10 ml – was passed through a column containing 1-2 g of Cationite SBS in the H-form at the rate of ~ 4 ml/minute; the column was then washed out with 8-10 ml lots of distilled water 3-4 times, and filtrate + washes containing acid in an amount equivalent to the salt passed through the cation exchange resin, titrated from a micro-buret with 10 ml of alkali solution which was thereby standardized.

In one series, alkali freed from carbonate was titrated using phenolphthalein as indicator; in another series, using another alkali solution, titration was carried out using methyl orange as indicator. In each series of tests, the titer of the alkali as determined by the ion-exchange method was compared with that established directly by titration with oxalic acid for one alkali solution, or with hydrochloric acid for the other alkali solution.

The results obtained are given in Tables 1 and 2.

It is clear from these results that standardization of alkali by an ion-exchange method gives accurate enough results.

SUMMARY

The possibility has been studied, and results given for the standardization of alkali by titrating it with the acids liberated by passage of solutions of salts of known concentration through the cation-exchange resin SBS in the H-form. It has been shown that the accuracy of such a method is, in the main, satisfactory.

Received April 18, 1954

LITERATURE CITED

[1] Yu. Yu. Lure and N. A. Filippova, Factory Labs., 13, 532 (1947); 14, 159 (1948); 15, 771 (1949).

[2] L. M. Orlova, J. Anal Chem., 5, No. 6 (1950).

[3] I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis", Vol. II, 1952.

[4] V. V. Fedorova, Bull. All-Union Heat Engineering Inst., No. 2 (1946).

[5] D. I. Ryabchikov and M. M. Senyavin, J. Anal. Chem., 8, No. 4, 195 (1953) (T.p. 215)*.

---

[*] T. p. = C. B. Translation pagination.

BLANK
PAGE

THE BENZOATE METHOD OF ALUMINUM DETERMINATION

A. I. Ponomarev and A. Ya. Sheslolskaya

The A. A. Baikov Institute of Metallurgy, Academy of Sciences, USSR, Moscow

Determination of aluminum in minerals, rocks, and metallurgical products is a difficult problem for the analyst, since existing methods for aluminum determination require preliminary removal of interfering elements, and even then satisfactory results are not always obtained.

Of existing methods for aluminum determination, mention may be made of the following:

1. Precipitation of aluminum with ammonia [1]. This method is usually used in systematic analysis; the aluminum is precipitated by ammonia along with iron, titanium, zirconium, vanadium, phosphorus, and certain other elements. In these cases, the aluminum content is calculated by difference after determination of all the other elements present in the precipitate as the oxides R_2O_3.

This type of determination – "by difference" – cuts down the time taken for an analysis, but, it cannot be recommended, since all the errors of the other individual determinations of elements which compose the precipitate of R_2O_3, are reflected in the value of the aluminum calculated "by difference".

2. Determination of aluminum as hydroxyquinolate [2]. This method has several advantages as compared with precipitation by ammonia. The crystalline precipitate of aluminum hydroxyquinolate is readily filtered and washed. The precipitate is dried at 120-140°, and weighed as $Al(C_9H_6ON)_3$; thanks to its high molecular weight, the conversion factor from $Al(C_9H_6ON)_3$ to Al_2O_3 is favorable to getting more accurate results. When this method is used it is necessary to carry out a preliminary separation with cupferron of iron, titanium, zirconium, and vanadium, or to remove iron by means of electrolysis on a mercury cathode, since these elements react with hydroxyquinoline.

3. Determination of aluminum as phosphate [3]. This method is not distinguished by any special accuracy, since the precipitate of aluminum phosphate hydrolyzes on being washed and its composition accordingly, differs from the theoretical value.

Titanium, zirconium, and some other elements are also precipitated by ammonium phosphate and have to be removed accordingly. Trivalent iron is reduced beforehand to the divalent state in which form it is not precipitated by phosphate.

4. Pyridine, like ammonia, precipitates aluminum along with iron, titanium, etc [4]. The advantage of this method consists in the quantitative separation of aluminum, iron, titanium, zirconium, vanadium, phosphorus, and chromium from manganese, nickel, cobalt, zinc, calcium, magnesium, and the alkali metals. Excess pyridine does not exhibit a solvent effect on calcium hydroxide precipitates.

5. Ammonium benzoate, like pyridine, precipitates aluminum along with iron, titanium, and others, and quantitatively separates these metals from manganese, nickel, cobalt, calcium, magnesium, and the alkali metals [5, 6].

In the present work we applied the benzoate method to the determination of aluminum in the presence of iron.

Kolthoff and Stanger [6], used ammonium benzoate for precipitation of aluminum, iron, and chromium in a weak acetic acid medium in order to separate them from divalent elements.

The behavior of various elements toward ammonium benzoate is shown in Table 1.

We made use of the fact that divalent iron is not precipitated by ammonium benzoate, for developing a method for the determination of aluminum in the presence of iron.

TABLE 1

Precipitation of Various Elements by Ammonium Benzoate in Acetic Acid Media

Elements precipitated quantitatively	Color of precipitate	Elements precipitated partially	Color of precipitate	Elements which are not precipitated
Al^{3+}	White	U^{6+}	Yellow	V^{4+} V^{5+}
Cr^{3+}	Grey-green	Be^{2+}	White	Co^{2+} Ni^{2+} Mn^{2+} Zn^{2+}
				Ca^{2+} Ba^{2+} Sr^{2+} Mg^{2+}
Fe^{3+}	Orange	Ti^{3+}	Brown	K^{+} Na^{+}
Ti^{4+}	White	Pb^{2+}	White	NH_4^{+} Li^{+}
Zr^{4+}	White	Cu^{2+}	Blue	Fe^{2+}
Th^{4+}	White	Sn^{2+}	White	Cd^{2+}
Ce^{4+}	Yellow			Hg^{2+}
Bi^{3+}	White			Ce^{3+}
Sn^{4+}	White			

TABLE 2

Determination of Alumina in Standard Solutions of Alum

Amount taken		Al_2O_3 found	Relative
Fe_2O_3 in g	Al_2O_3 in g	in g	error in %
0.1	0.0958	0.0954	−0.42
0.2	0.0958	0.0958	0.00
0.5	0.0958	0.0961	+ 0.31
0.8	0.0958	0.0959	+ 0.10
1.0	0.0958	0.0964	+ 0.62

Sodium hydrosulfite $Na_2S_2O_4$, which proved particularly convenient in our case, was used as the reducing agent for iron.

Reduction of iron to the divalent state by sodium hydrosulfite takes place readily, and precipitation of aluminum can be carried out immediately. Reprecipitation of the precipitate leads to complete separation of aluminum from large amounts of iron.

Under the conditions described below, precipitation of aluminum by benzoate is very rapid and quantitative. The white, flocculent precipitate becomes more dense on heating, settles out rapidly, can be filtered readily (and washed), and, in contrast to precipitates of aluminum hydroxide does not require such a high calcining temperature.

A check on the calcined precipitates of aluminum oxide for contamination by iron (for a double precipitation of aluminum by ammonium benzoate) showed that the amount of iron in Al_2O_3 precipitates is insignificant and varies within the limits 0.1-0.3 mg.

The relative behavior of other elements during precipitation of aluminum by ammonium benzoate must be considered further.

Titanium is quantitatively precipitated by ammonium benzoate along with aluminum, and can be determined in the calcined and weighed precipitate of alumina, by the usual colorimetric method.

Chromium is partially precipitated; phosphorus in quantities not exceeding 1% as P_2O_5, is precipitated in insignificant amounts — of the order of 0.1-0.2 mg.

Quinquevalent vanadium is not precipitated by ammonium benzoate, but, during the reduction of iron with sodium hydrosulfite, vanadium is reduced to the quadrivalent state (and partially to the trivalent), and, as our experiments showed, in that form is quantitatively precipitated by ammonium benzoate.

Shemyakin [7], used the benzoate method for gravimetric determination of vanadium. For this purpose, he reduced quinquevalent vanadium to the quadrivalent state in hydrochloric acid solution with a saturated solution of ammonium sulfite, and then precipitated the vanadium with ammonium benzoate. The compound thus obtained $[VO(C_6H_5CO_2)_2]$ was calcined and weighed as V_2O_5.

The analytical procedure described below was developed on the basis of preliminary experimental results (Table 2), and on a check on the method of precipitating aluminum with ammonium benzoate on standard samples of iron ores and slags (Table 3).

TABLE 3

Determination of Alumina in Ores and Industrial Products

Sample	Weight in g	Al_2O_3 content in %	Al_2O_2 found in %	Relative error in %
Iron ore	0.5	5.57	5.56	−0.18
(C. O. No 2)	0.5	5.57	5.57	−0.00
	0.5	5.57	5.53	−0.72
Slag (C. O. No 79)	0.5	6.65	6.64	−0.16
	0.5	6.65	6.61	−0.61
	0.5	6.65	6.78	+ 1.95

0.5-1 g (according to the expected aluminum content) of test rock, iron ore, or slag is placed in a platinum crucible, mixed with six times its amount of anhydrous sodium carbonate and fused in a gas burner. The melt is dissolved and silicic acid removed as usual. The residue, after treatment of the calcined silica with HF + H_2SO_4, is fused with the minimum amount of potassium pyrosulfate; this melt is dissolved in hydrochloric acid and combined with the filtrate obtained previously from the silicic acid.

When iron ore is analyzed, the test aliquot is decomposed initially in a beaker by heating with hydrochloric acid. The insoluble residue is filtered off, washed with hot water, ashed, and fused in a platinum crucible with anhydrous sodium carbonate. The melt is leached out with hot water, with simultaneous neutralization of hydrochloric acid, combined with the original filtrate, and silicic acid removed as usual.

To the filtrate which has a volume of 100 ml is added 2 g of ammonium chloride; the solution is then neutralized by addition of ammonia with continuous stirring, until a permanent turbidity is obtained on addition of one drop of ammonia in excess. 1 ml of concentrated acetic acid is next added; trivalent iron is reduced to the divalent state with sodium hydrosulfite which is added on a spatula tip in small portions as the dry salt, the solution being stirred until it becomes colorless.

After reduction of iron a 5% solution of ammonium benzoate is added, at the rate of 40 ml/0.1 g of aluminum oxide; solution + precipitate are carefully mixed and a small amount of macerated paper added, mixing is renewed, and then, after covering the beaker with a watch glass, it is placed on a water bath for 15 minutes.

To accelerate coagulation of the precipitate, the solution is mixed from time to time, until the liquid above the precipitate becomes transparent*. The precipitate is filtered immediately through a filter paper — white ribbon quality — washed 5 times with hot wash liquor (5 ml of 5% ammonium benzoate solution and 1 ml of concentrated acetic acid in 100 ml water). The beaker in which precipitation has been carried out is placed under the funnel, the precipitate on the filter paper is dissolved in 10% hydrochloric acid, the filter paper is carefully washed with hot water and precipitation of aluminum with ammonium benzoate repeated again as described above.

The filter paper containing macerated paper + sulfur is rejected. The reprecipitated precipitate is filtered through a new filter paper, washed 8-10 times with hot wash liquor. Filter paper + precipitate are placed in a weighed platinum crucible, ashed, calcined at 800-900°, and weighed as Al_2O_3. If titanium is present in the test sample, then the weight of calcined precipitate will be equal to $Al_2O_3 + TiO_2$. In this case the calcined and weighed precipitate of aluminum oxide is fused with sodium or potassium pyrosulfate, the melt dissolved in 5% sulfuric acid, and titanium determined colorimetrically with H_2O_2. The weight of TiO_2 is subtracted from the total weight of precipitate.

Determination of aluminum by this method can also be carried out in the general course of analysis, on an aliquot part of filtrate after removal of silicic acid, or on the precipitate of the sesquioxides.

---

* Usually, when there is a large amount of iron present in a test sample, an insignificant amount of the latter is oxidized during heating on the water bath. As a result, a yellow film of ferric oxide appears on the surface of the solution. It is recommended that another pinch of sodium hydrosulfite be added before filtration, to reduce the oxidized iron.

SUMMARY

1. A gravimetric method has been developed for determination of aluminum in the presence of iron in ores, minerals, and industrial products; it is based on precipitation of aluminum by ammonium benzoate in a weak acetic acid medium. Iron is reduced to the divalent state by sodium hydrosulfite and in that state does not interfere with aluminum determination.

2. The method is fairly rapid and permits determination of aluminum in the presence of large amounts of iron.

Received February 10, 1955

LITERATURE CITED

[1] A. I. Ponomarev, "Methods for the Chemical Analysis of Minerals and Rocks", Vol. 1, Acad. Sci. Press, 1951, p. 54.

[2] R. Berg, "The Use of Hydroxyquinoline in Analytical Chemistry" Gen. Sci. Tech. Press, 1937.

[3] V. F. Gillebrand and G. E. Lendel, "Practical Textbook on Inorganic Analysis", Gen. Sci. Tech. Press, 1937, p. 438.

[4] E. A. Ostroumov, "New Methods of Chemical Analysis based on the Use of Organic Bases", State Geol. Press, 1952.

[5] J. M. Kolthoff, V. A. Stenger, and B. Moskovitz, J. Am. Chem. Soc., 56, 812 (1934).

[6] V. A. Stenger, W.R. Kramer and A.W. Beshgetoor, Ind. Eng. Chem. Anal. Ed. 14, 797 (1942).

[7] F. M. Shemyakin, Factory Labs., 11, 986 (1934).

QUANTITATIVE DETERMINATION OF BORIC ACID, IRON, ALUMINUM SALTS WHEN ALL ARE PRESENT SIMULTANEOUSLY

M. B. Shchigol and N. B. Burchinskaya

Kiev Medical Institute

Determination of boric acid in the presence of heavy metals is of practical interest, since many boron-containing minerals such as, hydroboracite and ascharite contain up to 2% and more of Al_2O_3 and Fe_2O_3.

This problem has hardly been touched upon in the literature. The majority of the methods described almost invariably boil down to preliminary removal of boric acid from the other compounds by the following means: 1) preparation and distillation of methyl borate, followed by saponification of the latter in the distillate by means of potassium hydroxide [1], or by the alkali earth hydroxides [2]. Subsequently, in the first case, boron is determined gravimetrically as B_2O_3, while in the other case, after reaction with hydrogen fluoride, boron is determined gravimetrically as KBF_4; 2) removal of iron, aluminum, chromium and other metals by electrolytic separation on a mercury cathode [3]; 3) by precipitation of heavy metals with freshly precipitated calcium carbonate [4], barium hydroxide [5], and also with phosphate in an acetic acid medium [6]; 4) by determination of boron in melts by means of the cation exchange resin SBS [7]. In the latter case, the solution of melt is passed through a column, boric acid passes completely into the filtrate where it is determined volumetrically.

All the methods enumerated, in the authors' opinion, are far from reliable; firstly, because they take a long time and are cumbersome; secondly, the analytical results are not reproducible. Thus, Mukhina and Alechin [8], after checking the metal borate and carbonate methods on steels containing up to 0.05% boron, concluded that the methyl borate method only gives satisfactory results after 5-6 distillations, while, when the carbonate method is used, up to half the boron is lost.

Thus, there is no reliable published method which permits determination of heavy metals and boric acid when these are present simultaneously. A potentiometric technique for determining iron and aluminum with the help to of tetraborate[9], is the basis of the proposed method of determining iron, aluminum, and boric acid, when they are all present simultaneously.

Investigations were carried out along the following lines:

1) titration of mixtures (solutions of aluminum salts and boric acid, ferric salts and boric acid) with alkali, both volumetrically, and potentiometrically, was studied; 2) titration of the same mixtures with borax was studied; 3) determination of iron and aluminum salts, and of boric acid boratometrically was studied.

All starting materials were doubly recrystallized, while iron salt solutions were prepared in dilute hydrochloric acid.

It is known from published results, and we also confirmed it experimentally ourselves, that alkali solutions cannot be used for determination of such systems as $Al^{3+}—H_3BO_3$, $Fe^{3+}—H_3BO_3$, etc. Errors in such cases can amount to 10% and more, the error increasing with increasing metal ion concentration.

The borate method [9], permits quantitative determination of aluminum and iron in the presence of any amount of boric acid with sufficient accuracy. Titration is carried out with 0.1 N borax potentiometrically using a Pt/Pt black electrode as indicator electrode, or volumetrically, using methyl red as indicator. In the latter case, determination is only possible up to a definite concentration limit for the iron salt ($4 \cdot 10^{-3}$ mol/liter). At higher concentrations titration becomes difficult on account of the increasing color of the iron borate formed. The amount of boric acid in such mixtures is found as follows: to a known volume of mixture is added that amount of 0.1 N borax which is required for combining with the aluminum (iron) ions, and an equal volume of glycerol, the mixture obtained is titrated with 0.1 N sodium hydroxide using phenolphthalein as indicator. Glyceroboric acid and also iron and aluminum tetraborates are thereupon titrated. The amount of boric acid is determined by difference.

Calculation is based on the formula $A-2B^{*}=C$, where A = ml of 0.1 N NaOH; B – the number of ml of 0.1 N $Na_2B_4O_7$ used for titrating the metal salts; C – the number of ml of 0.1 N H_3BO_3. Results are given in Table 1.

TABLE 1

Composition of mixture	Amount taken in $g \cdot 10^3$	Amount found in $g \cdot 10^3$	Error in $g \cdot 10^3$	Composition of mixture	Amount taken in $g \cdot 10^3$	Amount found in $g \cdot 10^3$	Error in $g \cdot 10^3$
Al^{3+}	0.8118	0.8110	−0.0018	H_3BO_3	35.265	35.226	−0.039
H_3BO_3	30.90	30.92	+ 0.020	Fe^{3+}	0.2607	0.2620	+ 0.013
Al^{3+}	0.2025	0.2016	−0.0009	H_3BO_3	176.340	176.328	−0.012
H_3BO_3	30.90	30.85	−0.005	Fe^{3+}	10.430	10.437	−0.007
Al^{3+}	0.4050	0.4032	−0.0018	H_3BO_3	7.053	7.055	+ 0.002
H_3BO_3	30.90	30.92	+ 0.020	Al^{3+}	0.457	0.0456	+ 0.001
Al^{3+}	0.834	0.830	−0.004	Fe^{3+}	1.75	1.73	−0.02
H_3BO_3	12.86	12.80	−0.060	H_3BO_3	6.2	6.17	−0.03
Fe^{3+}	1.043	1.045	+ 0.002	Al^{3+}	0.914	0.916	+0.002
H_3BO_3	0.705	0.736	−0.031	Fe^{3+}	0.840	0.838	−0.002
Fe^{3+}	1.043	1.043	—	H_3BO_3	6.2	6.22	+0.02

Where aluminum and iron salts, as well as boric acid are all present simultaneously, determination is carried out as follows: a known volume of test mixture is transferred to a 100 ml beaker, the volume is made up to 25 ml with water and the whole titrated potentiometrically with 0.1 N borax, using a Pt/Pt black electrode as indicator electrode. When this is done, two jumps are observed on the titration curve, the first indicates the end point for titration of ferric ions (A ml) ($K_{[Fe_2(B_4O_7)_3]}$ of the order of 10^{-15}), while the second jump corresponds to the end point for titration of total iron + aluminum (B ml) ($K_{[Al_2(B_4O_7)_3]}$ of the order of 10^{-11}). The potentiometric curve obtained is shown in the diagram. The aluminum is determined by the difference (B−A).

Boric acid is determined in the mixture as described already.

It is evident that the presence of boric acid does not interfere with titration of aluminum and iron salts by borax. This, obviously, is only true when the pH of the solution after the equivalence point during titration with borax of mixtures of aluminum (iron) salts with boric acid, and during titration of pure solutions of aluminum (iron) salts, coincide. In actual fact, the mean experimental pH value of the solution in the latter case is approximately equal to 6.8. At the same time, theoretical calculation of the pH of a buffer solution containing 0.04 ml of 0.1 N borax (i.e. the amount which leads to a sharp increase in electrode potential) gives a value of 6.84 when 5 ml of 0.1 N boric acid $[H^+] = K_k \frac{c_k}{c_c}$, is present, while when 10 ml of 0.1 N boric acid is present the pH is 6.54. Consequently, use of a borax solution permits quantitative determination of heavy metal salts and boric acid when they are present simultaneously with sufficient accuracy.

Of great practical interest is determination of aluminum (iron) salts and boric acid in the presence of a mineral acid. Various mixtures with constant metal and mineral acid (HCl) contents respectively, and increasing amounts of ~ 0.1 N boric acid, were prepared for a study of this problem.

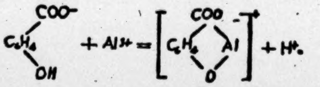
Determination of Aluminum-Borate Mixtures

a) To 2 ml of a mixture containing 1.1 ml of 0.1 N aluminum nitrate and 0.32 ml of 0.1 N hydrochloric acid, was added 2-5 ml of 0.108 N boric acid. The mixture obtained could be titrated with 0.1 N borax, both potentiometrically using a Pt/Pt black electrode as indicator electrode, and volumetrically using methyl orange as indicator. In this case total mineral acid + aluminum salt was titrated (A ml).

b) To the same volume of original mixture was added 3-5 ml of 0.1 N sodium salicylate, and the whole titrated with 0.1 N borax, using methyl red as indicator. Here, mineral acid and 2/3 of the original amount of aluminum salt was titrated (as a result of the formation of an inner complex compound) [10, 11] (B ml).

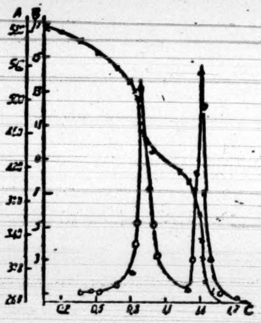
---

* 1 ml of 0.1 N borax is equivalent to 2 ml of 0.1 N H_3BO_3.



The amount of aluminum was determined from the first two determinations by means of the formula $3(A-B) = C$ ml of 0.1 Al^{3+} solution.

The amount of mineral acid is given by A−B.



Titration curve for a mixture of 0.94 ml of 0.1 N $FeCl_3$, 0.508 ml of 0.1 N $Al(NO_3)_3$ and a ml of 0.1 N H_3BO_3 with 0.107 N $Na_2B_4O_7$.
A) measured potential (in mV) relative to the saturated calomel electrode; B) mV potential change (in mV/0.01 ml); C) volume of $Na_2B_4O_7$ (in ml).

c) Free boric acid in the mixture was determined as follows; to the same volume of mixture was added 0.1 N borax in an amount sufficient to combine with the aluminum and free mineral acid (A ml), and an equal volume of glycerol, and the whole titrated with 0.1 N alkali, using phenolphthalein as indicator (D ml).

The amount of boric acid is given by D−2A.

Sodium oxalate solution can also be used with considerable success for determining free mineral acid in this mixture. The following procedure was adopted in this case; to a known volume of test mixture was added a 10-fold excess of ~. 0.1 N $Na_2C_2O_4$, and the whole titrated with 0.1 N borax (or NaOH) using methyl red as indicator [12] (E ml). The oxalate complexes of iron and aluminum are more stable than the corresponding borate complexes, thus, in particular, $K_n \cdot [Fe(C_2O_4)_3]^{3-} = 1.2 \cdot 10^{-24}$ [13].

In this case the amount of aluminum is given by the difference A−E. Free boric acid in the mixture was determined as described already. Results are given in Table 2.

TABLE 2

Composition of mixture	Amount taken in $g \cdot 10^3$	Amount found in $g \cdot 10^3$	Error in $g \cdot 10^3$	
Al^{3+}	1.035	1.00	−0.035	
H_3BO_3	13.353	13.170	−0.183	1:13
HCl	1.17	1.20		
Al^{3+}	1.035	1.01	−0.025	
H_3BO_3	33.38	33.1720	−0.2108	1:34
HCl	1.17	1.18		
Al^{3+}	0.520	0.525	+0.0050	
H_3BO_3	13.353	13.200	−0.1530	
HCl	1.17	1.15		
Fe^{3+}	.0218	4.0230	+0.0020	
H_3BO_3	1.3353	1.3413	+0.0060	4:1
HCl	2.044	2.051		
Fe^{3+}	2.0109	2.0133	+0.0024	
H_3BO_3	33.3828	33.3906	+0.0078	1:16
HCl	1.022	1.030		
Fe^{2+}	0.5025	0.5118	−0.0093	
H_3BO_3	166.910	166.80	−0.1100	
HCl	0.255	0.240		1:330
Al^{3+}	0.457	0.450	−0.007	
Fe^{3+}	0.840	0.820	−0.020	
H_3BO_3	6.20	6.30	+0.100	
HCl	3.50	3.50		
Al^{3+}	0.900	0.902	+0.002	
Fe^{3+}	1.680	1.68		
H_3BO_3	12.40	12.23	−0.17	
HCl	3.50	3.45	0.05	
Al^{3+}	0.450	0.452	+0.002	
Fe^{3+}	1.680	1.67	−0.01	
H_3BO_3	6.20	6.17	−0.03	
HCl	3.50	3.54	+0.04	

Determination of Iron — Borate Mixtures

For determination of iron-borate mixtures an acidified solution of ferric chloride containing 0.9 g $FeCl_3$ and 50 ml of 0.1 N HCl in 100 ml solution was prepared beforehand.

a) To 1 ml of this solution was added increasing amounts of boric acid and the mixture titrated with 0.1 N borax. The amount in ml of 0.1 N borax (A ml), used for titration corresponds to total iron + mineral acid.

b) Free mineral acid in the mixture was determined in the presence of $Na_2C_2O_4$ in the same way as that described for aluminum determination (E ml). The amount of iron was found from the difference A—E.

c) Free boric acid was determined as in the case of aluminum salts.

Results of determinations are given in Table 2.

Determination of Aluminum — Iron — Borate Mixtures

Here, as in previous cases, various mixtures with known concentrations of aluminum, iron, boric acid, and mineral acids were prepared:

a) A known volume of mixture was taken and to this was added a ten-fold excess of ~ 0.1 N $Na_2C_2O_4$, after which the free mineral acid in this mixture was titrated with 0.1 N borax using methyl red as indicator (A ml).

b) The same volume of mixture was potentiometrically titrated with 0.1 N borax using a Pt/Pt black electrode as the indicator electrode. Two jumps were obtained on the titration curve; the first jump (B ml) corresponded to total mineral acid + iron; while the second jump (C ml), corresponded to total mineral acid + iron + aluminum.

The difference C—B gives the aluminum.

The amount of iron is given by B—A.

c) Boric acid in the mixture was determined, as described already.

Results are given in Table 2.

SUMMARY

1. The borate method which we have proposed previously for the determination of aluminum and iron, enables these two metals to be determined in the presence of boric acid, with sufficient accuracy.

2. A variant is suggested for the quantitative determination of boric acid, aluminum and ferric ions, both in neutral media, and also in the presence of a mineral acid, when all are present simultaneously.

Received January 27, 1954

LITERATURE CITED

[1] Fadeev, Z. anorg. Chem., 36, 568 (1897).

[2] F. Gooch, and L. Jones, Z. anorg. Chem., 19, 417 (1899).

[3] H. Chizhevsky, Ind. Eng. Chem., 18, 607 (1926).

[4] E. Wherry and W. Shapin, J. Am. Chem. Soc., 30, 1867 (1908).

[5] A. E. Sabinina and T. B. Stonkel, Factory Labs., 7, 752 (1947).

[6] H. Funk and H. Winter, Z. anorg. Chem., 142, 257 (1928).

[7] A. I. Lazarev, Factory Labs., 6, 666 (1952).

[8] Z. S. Mukhina and A. F. Aleshin, Factory Labs., 11, 1 (1945).

[9] M. B. Shchigol and N. B. Burchinskaya, J. Anal. Chem., 5, 289, (1952) (T. p. 325)*.

[10] Bruns, Z. anal. Chem., 55, 321 (1916).

---

* T. p. = C. B. Translation pagination.

[11] A. K. Babko, J. Gen. Chem., 9, 1624 (1940).

[12] A. K. Babko, Factory Labs., 8, 891 (1935).

[13] V. F. Toropova, J. Gen. Chem., 11, 1211 (1941).

BLANK
PAGE

DETECTION OF BERYLLIUM WHEN NO PRECIOUS METAL VESSELS ARE AVAILABLE

E. P. Ozhigov and T. I. Vedernikova

Far East Section of the USSR Academy of Sciences

Detection of beryllium is based on fusion of ores and minerals of this element which are difficult to decompose, with strongly reactive fusion mixtures such as: alkali hydroxides, potassium bifluoride, potassium bisulfate, etc.

Apart from the fact that such methods require the use of beakers made from such scarce metals as platinum and silver, they also have the drawback of requiring many operations for removing elements which interfere with beryllium determination. When solid alkali hydroxides are used as the fusion agent, fusion must be carried out in silver crucibles. This operation is often accompanied by spitting of the alkali, and is carried out at a lowered temperature, since even slight overheating may lead to damage of the crucible. Beryllium is determined in the alkali solution after separation of iron and to some extent of calcium, magnesium, etc. [1], as hydroxides.

A more convenient method seems to be that suggested by Feigl and Schaeffer recently [2], in which test material is fused in a platinum beaker with potassium bifluoride, as a result of which a readily soluble complex compound of beryllium is formed – potassium fluoroberyllate – according to the following approximate scheme:

$$Be_2SiO_4 + 8HF \rightarrow 2BeF_2 + SiF_4 + 4H_2O;$$

$$BeF_2 + 2KF \rightarrow K_2BeF_4.$$

By leaching the melt out with water, potassium fluoroberyllate (K_2BeF_4), dissolves, while the cryolite of iron and aluminum (K_3FeF_6 and K_3AlF_6), as well as the fluorides of magnesium and calcium, which are sparingly soluble in water, particularly in the presence of sodium or potassium fluoride, remain undissolved.

In most cases, irrespective of the method used for decomposing minerals containing beryllium, this metal is detected in the alkaline solution by means of its reaction with quinalizarin. As we showed experimentally, this method is inapplicable when the original material contains significant amounts of copper or nickel; these metals form fluorides which are appreciably soluble in water, and lead to reddening of the alkali solution of quinalizarin in the case of copper – and to an increase in the blue color of the solution, in the case of nickel. When test minerals, or ores, are fused with potassium bifluoride in iron and not platinum beakers, not only does this lead to economy of precious metals, but it has been found that it opens up the possibility of determining beryllium in the presence of appreciable amounts of copper and nickel.

Beryllium containing minerals are decomposed not only by potassium bifluoride, but also by the iron cryolite formed on the walls of the beaker. It is known [3], that iron cryolite reacts preferentially with beryllium in the mineral, and does not react with the oxides of silicon, aluminum, and iron present:

$$3BeO + 2K_3FeF_6 = 3K_2BeF_4 + Fe_2O_3.$$

Elements which are present in solution and interfere with beryllium determination, are also removed.

In accordance with the values of the standard potentials or the activity series of the metals, copper (or any other metal, less active than iron) separates out on the walls of the iron beaker according to the following reaction:

$$Fe + CuF_2 \rightarrow Cu + FeF_2.$$

Iron is further oxidized to ferric iron, and, in the presence of excess sodium fluoride, forms the insoluble cryolite.

As I. V. Tananaev [4], has shown, iron ions can be completely precipitated from solution by sodium fluoride which converts them into an insoluble form. This permits beryllium to be determined in the presence of any amount of iron.

TABLE 1

Fusion conditions	BeO content of test samples			Color of a drop of solution after it has been made alkaline and reacted with quinalizarin	
	Parts percent	in %	Amount determined in μg/ml	In a platinum beaker	In an iron beaker
Ore 0.005-0.01 g KHF_2-0.03 g	Tenths	0.491; 0.31; 0.29 0.25	15; 14; 12	Blue	Dark blue and blue
		0.17; 0.15; 0.12; 0.14	8; 6; 7	Blue and light blue, sometimes with a violet shade	Blue
	Composition	0.07; 0.05; 0.04; 0.06	3.5; 2.5; 2.0; 1.5	Light blue with a lilac shade	Light blue

TABLE 2

Ore – 0.005 g; CuO or NiO – 0.001 g; KHF_2 – 0.05 g

Content in %			Color of a drop of solution after it has been made alkaline and reacted with quinalizarin	
BeO	CuO	NiO	In a platinum beaker	In an iron beaker
0.14	16.6	–	Not determined because of reddening of solution	Dark blue
0.25	16.6	–	"	Blue
0.05	16.6	–	"	Blue
0.41	–	16.6	Intense blue color because of nickel	Dark blue
0.25	–	16.6		Blue
0.05	–	16.6		Blue

It was shown in preliminary experiments that fusion of test ore with potassium bifluoride proceeds quite well in small iron beakers 6 cm in diameter; beaker corrosion is comparatively small so that a large number of determinations can be barried out in one beaker. Fusion temperature was 550°.

Analytical results for ores of very complex composition (containing the minerals $Be_3Al_2Si_6O_{18}$ – beryl; $BeAl_2O_4$ – chrysolberyl and Be_2SiO_4 – phenacite) are given in Table 1.

Reaction sensitivity was established by repeated dilution with water of 2 ml of solution leached from a beaker and filtered, and containing 0.4 μg in 1 ml of test solution, using beakers made from both iron and platinum respectively. The following series of tests were carried out in order to check on the effect of addition of cupric and nickel oxides on the color of the alkaline quinalizarin solution. Copper was introduced in the form of chemically pure cupric oxide; nickel oxide was obtained by decomposition of chemically pure nickel nitrate.

Taking into account the solubility of nickel fluoride in water, and its slow separation from solution on to the iron, and also the possibility of formation of complex compounds with ammonia [5], leaching was carried out, not with water, but with 0.25 N NaOH (after filtration of the precipitate) to guarantee that no nickel ions get into solution. Results are given in Table 2.

These results show that the use of iron crucibles for fusion prevents copper from getting into solution, while extraction with 0.25 N alkali prevents formation of soluble nickel ions in the solution. Reaction sensitivity drops in the presence of nickel and copper and amounts to 0.6 μg in 1 ml of test solution.

Analytical Procedure

A few mg of test material is fused with three or five times its amount of potassium bifluoride in an iron crucible for 3 minutes. After cooling, the mass is leached with 2 ml of water (or 2 ml of 0.25 N NaOH, if there is much nickel) and the solution filtered through a small filter. A drop of the transparent liquid is placed on a white porcelain plate, which has been treated with paraffin and to the drop is added a drop of a solution of quinalizarin in ammonia* . At the same time, a test with water or alkali is carried out alongside. If beryllium is present, in the test material, then, depending on the amount, the drop will be colored blue, sometimes with a small amount of colored precipitate. Since the ammoniacal quinalizarin is often violet and insignificant amounts of beryllium are only detectable with difficulty, it is necessary to add a drop of bromine water to both the drop of test solution and the drop of blank, after addition of quinalizarin. If there is no beryllium in the drop, decolorization starts sooner, since the compound of quinalizarin with alkali is less stable than the beryllium quinalizarin complex in alkali solution.

SUMMARY

1. It has been shown that Feigl and Schaeffer's method of detecting beryllium is inapplicable to ores containing appreciable amounts of copper and nickel.

2. A simple method has been proposed for detecting beryllium when no precious metals beakers etc. are available; substitution of such beakers by iron ones does not lead to a loss of sensitivity and specificity.

3. The method is suitable for geological prospecting parties for field use.

Received August 15, 1953

LITERATURE CITED

[1] V. A. Nazarenko and N. S. Poluetkov, "Semi-micro Chemical Analysis of Ores and Minerals, State Chem. Press, 1950.

[2] Feigl. and Schaeffer. Anal. Chem., 23, 2, 350 (1951).

[3] H. C. Kawecki. Frans. Electrochem. Soc., 89, 183 (1946).

[4] I. V. Tananaev and E. N. Diechman, Factory Labs., 12, No. 1 (1946).

[5] N. I. Blokh. "Qualitative Chemical Analysis", State Chem. Press, 1952.

---

* 50 mg of quinalizarin is dissolved in 100 ml of 10% ammonia. The solution is only usable for 2 hours.

BLANK
PAGE

BRIEF COMMUNICATIONS

A NEW METHOD OF DETECTING CARBON

B. M. Gladshtein

There are only a limited number of methods at the organic chemist's disposal for detecting carbon in compounds; at the same time, the necessity often arises in the course of synthetic work of establishing whether or not a given compound is organic in nature.

The generally adopted methods of determining carbon (combustion with cupric oxide, ashing) very often present considerable difficulties, particularly in the case of compounds containing small amounts of carbon, or in the case of those which on combustion yield acid anhydrides, or compounds which contain elements which yield non-volatile oxides. It would be convenient if one could use a color reaction for detecting carbon, which would be specific for this element. We chose Berlin Blue (ferric ferrocyanide), used by Lassaigne* for detecting nitrogen in organic compounds.

The suggested method consists in heating a mixture of test material with ammonium chloride and potassium or sodium metal. In a high melting glass test tube is placed a mixture of a few mg of test material with an equal amount of ammonium chloride, and the whole heated with a small bead of sodium or potassium metal. If the test material contains carbon, sodium or potassium cyanide will be formed. The procedure subsequently followed is similar to the Lassaigne technique for nitrogen determination. The red-hot tube is placed in a beaker containing some water (10-20 ml). (Care should be taken at this juncture). The contents of the broken tube are macerated with the water. A few ml of the solution obtained is filtered into a test tube, two drops of a solution of Mohr's salt is added and the same amount of ferric chloride; the contents of the tube are heated to the boil, cooled, and acidified with hydrochloric acid. If the test material contains carbon, the solution will have a blue or green color. A yellow color only testifies to the absence of CN^-, and not necessarily to the absence of carbon. When compounds which contain sulfur are analyzed, CNS^- can be formed, its presence being shown by a reaction with ferric chloride.

The reaction described has been tested on carbohydrates, hydroxy compounds, organo-mercury compounds, and other representatives of various classes of elemental organic compounds. The reaction is also applicable to the determination of carbon in inorganic materials which contain carbon.

The sensitivity is obviously similar to that of the Lassaigne method for nitrogen.

Received February 4, 1955

---

* Lassaigne, Ann., 48, 367 (1843).

BLANK
PAGE

CHRONICLE

ACADEMICIAN SERGEI IVANOVICH VAVILOV AND HIS ROLE IN THE DEVELOPMENT OF LUMINESCENT ANALYSIS

(In commemoration of his death five years ago)

January 25, 1956 marks the fifth aniversary of the death of Academician Sergei Ivanovich Vavilov, a prominent scientist and a fine man. S. I. Vavilov was a physicist and optician whose distinguished work in these fields was well known to the scientific community.

However, the valuable contributions of this exceptional scientist have not, as yet, been adequately described in the chemical literature. S. I. Vavilov was one of those scientists with a broad range of interests, whose creative efforts transcend their narrow scientific specialties and greatly accelerate the development of related fields of knowledge. This was particularly so in the case of luminescent analysis, only one of the many fields which are indebted to S. I. Vavilov's diverse theoretical and practical researches. We see in this case with exceptional clarity how Vavilov's ability to combine the theoretical with the practical enabled him to use scientific achievements for concrete ends in every-day life and apply them, in practice, for the benefit of the nation.

"Up to October* , the number of physicists, chemists and engineers in Russia, specializing in the field of luminescence, could be counted on the fingers of one hand" [1]. S. I. Vavilov said this in 1946 at a conference on luminescence in which hundreds participated. "Development in the field of luminescence was hindered by the absence of a correct theoretical foundation..." [2].

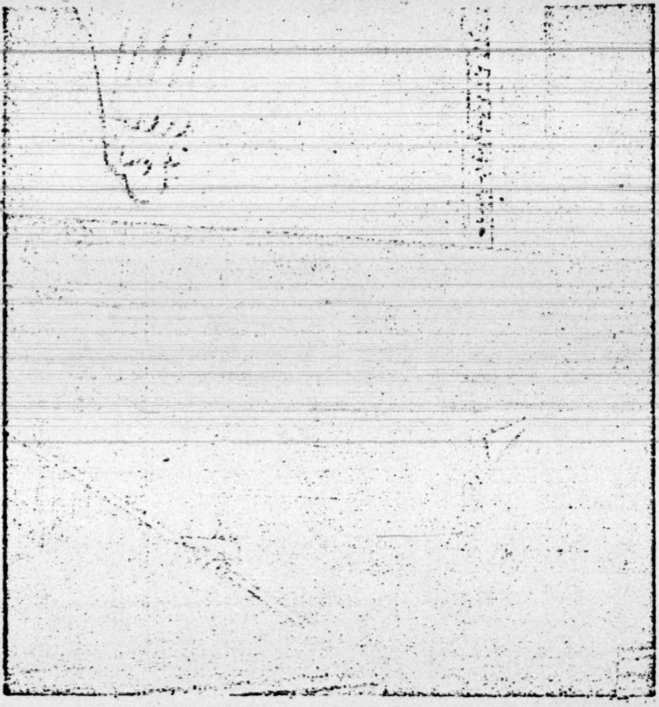
The researches of S. I. Vavilov and his school were instrumental in the establishment of such a theoretical foundation. In the twenties, S. I. Vavilov was the first to determine experimentally how large a portion of luminous energy is absorbed by fluorescent dyes and then emitted in the form of fluorescence; he proved that, contrary to common belief, this portion is not small but reaches 80-90%. The phenomenon of luminescence began to attract universal attention. It is noteworthy that even then, S. I. Vavilov had declared that the creation of luminescent sources of illumination was possible.

"An understanding of luminescence, even in its barest outlines, became possible only since the discovery of the quantum nature of light and matter, i.e. since the beginning of the 20th century" [2].

S. I. Vavilov, the author of the above statement, made a decisive step in this direction; he measured the variation of the yield of fluorescence as a function of the wave length of the exciting light [3]. S. I. Vavilov investigated the variation of the ratio of the fluorescent energy emitted to the luminous energy absorbed when fluorescence was excited by light of various wave lengths. It turned out that the energy yield increases linearly with increase in wave length of the exciting light, or in other words, the portion of luminous energy which is emitted in the form of fluorescent radiation increases as the wave length of the exciting light approaches the wave length of the fluorescent radiation. In terms of quanta, this means that whether fluorescence is excited by light with a shorter wave length with larger quanta (for example ultra-violet light) or by light with a longer wave length with smaller quanta (for example blue), for the same number of quanta absorbed, the same number of quanta will be emitted as fluorescent radiation, that is, the quantum yield is constant. Therefore, the ratio of emitted energy to absorbed energy more closely approaches unity as the emitted and absorbed quanta more closely correspond in magnitude, i.e. the more closely the wave length of the exciting light coincides with the wave length of the fluorescent radiation. The surplus energy of an exciting quantum with respect to an emitted quantum is consumed in intramolecular oscillations and finally converts to heat [4].

---

* The October R volution is apparently meant (Tr. note).



Academician Sergei Ivanovich Vavilov.

To Academician Vavilov, the constancy of the quantum yield was not merely a chance empirical relationship which he had come upon during his investigations. S. I. Vavilov perceived the existence of a fundamental law of photoluminescence which revealed the essential nature of the phenomenon.

Later, S. I. Vavilov and his school established other laws for the conversion of absorbed luminous energy to fluorescent radiation, and thus created a firm foundation for the development of luminescent analysis. Without an understanding of the nature of the phenomenon, it was impossible to employ it for analytical purposes, to forsee the complications involved in its use, or accurately to evaluate analytical problems and methods. It is not a chance occurrence that in order to solve the pressing, theoretically and practically important problem which then faced geophysicists, i.e. the determination of the ozone content of the upper atmospheric strata and the clarification of the concentration variation gradient at various altitudes, S. I. Vavilov designed a method for utilizing luminescent analysis. In his laboratory he worked on a luminescent method of determining atmospheric ozone. This was in the thirties, when the possibility of using luminescent analysis as a method of chemical analysis was disputed or at least considered debatable.

In one of his statements, S. I. Vavilov evaluated luminescent analysis as follows: "What advantage does luminescent analysis have over absorption analysis? Its advantage is chiefly found in the characteristics of the human eye, the extreme sensitivity of which is known to closely approach the maximum in its amazing ability to perceive color gradations and, finally, in its ability to form images" [5].

In his paper (in collaboration with Sveshnikov) on the application of luminescent analysis in medicine [6], S. I. Vavilov emphasized that exceptional sensitivity is the distinguishing characteristic of luminescent analysis.

S. I. Vavilov's evaluation proved correct. At present, when a substance is investigated, its luminescent properties are utilized as well as all its others. Chemical luminescent analysis has already found wide application. Fluorescence is no longer considered to be a property so variable and dependent on unknown influences that it is impossible to use it for chemical analysis and, in particular, for quantitative analysis. A thorough understanding of the phenomenon of fluorescence was attained in the last decade due in great part to the researches of Academician Vavilov and his school of Soviet physicists, and assures further progress in the utilization of luminescent analysis; now the problem is to correctly devise controls, taking into consideration the distinctive nature of the phenomenon of luminescence and also those laws which have been established in this field. Without discussing them in detail, we present the following general relationships which form the basis of chemical luminescent analysis.

1. The luminescence of any substance is a characteristic, individual property; in particular, the fluorescent spectrum and the "yield" are independent of the wave length of the exciting radiation; despite this, the brightness of the illumination is terminally small, when the fluorescence is excited by light which is only weakly absorbed.

2. Substances which have acid or basic properties and whose electronic structure changes with pH usually exhibit parallel changes in their fluorescent properties; molecules and ions can be distinguished both by their radiation spectrum and by the intensity of the latter. We have a complete analogy here with changes in color of organic materials with the medium. From this fact arises the possibility of using fluorescent indicators for carrying out titrations and for determining pH in colored media. Th [illegible]

3. The fluorescence of certain substances increases when their molecules are adsorbed on a solid surface or placed in a viscous medium.

4. The brightness of the fluorescence of a solution is determined basically by two factors: how much light is absorbed in the layer under observation, and how much of this light is converted into luminescent radiation, i.e. the yield. In the general case, A, the amount of light absorbed is given in the following equation:

$$A = S\,[1 - Ie^{-\epsilon cd}] = S \cdot I\,[1 - e^{-\epsilon cd}] .$$

where I is the intensity of the incident light; ϵ is the absorption coefficient of the solution; c is the concentration, d is the thickness, and S is the area of the absorbing layer.

Nevertheless, if the concentration of the solution is low and the light flow passing through the layer is weakened by not more than ~ 10%, then on resolving $e^{-\epsilon cd}$ into a series

$$\left(e^{-\epsilon cd} = 1-\epsilon cd+\frac{(\epsilon cd)^2}{1\cdot 2}-\frac{(\epsilon cd)^3}{1\cdot 2\cdot 3}\cdots\right)$$

it is possible to disregard all members after the first two; i.e., under such conditions the amount of light absorbed by a layer of solution is proportional to its concentration; consequently, the intensity of the solution fluorescence is also proportional to the concentration of fluorescing material as long as the yield is constant. Accordingly, quantitative fluorescent analysis is always carried out in dilute solution. At concentrations greater than ~ 10^{-4} – 10^{-5} g/ml, concentration extinction starts; the corresponding change of yield with increase in concentration is given by Vavilov's equation [7]:

$$\rho_c = \rho_0\cdot e^{-(c-c_0)k}.$$

from which it is clear that starting at a concentration of c_0, ρ_c – the yield at some concentration c is $e^{-(c-c_0)k}$ times less than ρ_0 – the yield for concentration c_0, and that with increasing concentration, and consequently with an increase in the difference $c-c_0$, the yield drops. S. I. Vavilov emphasized that at high concentrations, extinction increases even more rapidly; this equation is not applicable under such conditions.

5. If a fluorescent material reacts reversibly with a component present in solution, forming an easily dissociated non-fluorescing complex, then the intensity of the fluorescence of the solution will decrease, and, according to S. I. Vavilov's classification "extinction of the first type" takes place. Another type of extinction where the extinguisher is an impurity, and in which the impurity reacts with the excited molecules and deprives them of the capacity to give off the light energy they have absorbed as fluorescent radiation, is, on the other hand, called "extinction of the second type" by Vavilov. Vavilov quite clearly divided extinction processes into these two classes [8]; he and his coworkers developed an experimental method for establishing to which type any particular concrete case belongs. Thanks to this, the chemist is able to detect chemically reversible interaction between fluorescent material and an extinguisher. Thus, Weber using this very method, established formation of an unstable complex between riboflavin and purines, which exhibit a damping effect on the fluorescence of the former. On increasing the temperature, equilibrium is displaced towards dissociation of the complex, and the damping becomes weaker; in cases of extinction of the second type increases in temperature increases damping.

It is essential to take into account the possibility of the presence of damping impurities during quantitative fluorescent analysis. In this connection, reference standards are sometimes prepared in the same multi component media as the test solutions themselves.

In certain cases, damping of fluorescent can be used for suppressing harmful luminescence, e.g. for destroying background fluorescence.

6. Fluorescent reactions are widely used now which make it possible to convert non-fluorescent compounds into fluorescent ones, and by means of the luminescence of these compounds it is possible to detect and determine quantitatively such compounds. There is, as yet, no complete understanding of the relation between the structure of a material and its luminescent properties; reactions and reagents have to be chosen empirically, and one has to be satisfied with certain general theoretical principles, in the same way as is done at the moment in the search for color reactions.

7. If several components of a mixture exhibit similar fluorescence, it becomes necessary to separate them. For this purpose, paper chromatography is particularly suitable: on "spot" chromatograms it is possible to detect amounts of materials of the order of parts of a gamma; fluorescent observations help out in the development of such small amounts of material; the methods supplement each other.

The sensitivity with which observations of luminescence can be made, determines the exceptional efficiency of other types of luminescence analysis also. It is sufficient to point out the method developed in Vavilov's laboratory for sorting glasses under factory conditions, which is based on observation not only of fluorescence, but also of post-illumination, for the excitation of which ultra-violet light is used. Vavilov always emphasized that one should use exact physical methods of research in luminescent analysis, and not be satisfied with generally accepted observations of fluorescence in the visible. "All the wonderful possibilities of luminescent analysis are far from exhausted", said Vavilov at a conference on luminescence in 1948 [1].

From what has been said it is clear how much Vavilov has done for fluorescent analysis. He himself worked out many of the basic theoretical principles, on the basis of which it became possible to develop chemical luminescent analysis, he evaluated anew the possibilities of this type of analysis, he was the inspiration and organizer in this field. Vavilov gave a lot of attention to setting up the material basis for the development of luminescent analysis. He was also responsible for ensuring supplies of the requisite apparatus for work in this field, for issuing collections of reports on luminescent analysis and organizing conferences; our country is indebted to him for the rapid developments made in luminescent analysis.

M. Konstantinova-Shlezinger

LITERATURE CITED

[1] S. I. Vavilov, Bull. Acad. Sci. USSR, Phys. Series 13, 8 (1949). Introduction.

[2] S. I. Vavilov, Bull. Acad. Sci. USSR, Phys. Series 9, 278 (1945). Introduction.

[3] S. I. Vavilov, Z. Phys. Chem., 42, 311 (1927).

[4] S. I. Vavilov, Bull. Acad. Sci. USSR, Phys. Series 9, 283 (1945).

[5] S. I. Vavilov, Bull. Acad. Sci. USSR, Phys. Series 13, 241 (1949). Introduction.

[6] S. I. Vavilov and B. Ya. Svechnikov, "Luminescent Analysis in Medicine" Medical News II, 3 (1940).

[7] S. I. Vavilov, Z. Phys. Chem., 31, 750 (1925).

[8] S. I. Vavilov, Proc. Acad. Sci. USSR, 3, 271 (1936).

BLANK
PAGE

INTERNATIONAL CONGRESS ON ANALYTICAL CHEMISTRY

From the 9th to the 16th of September 1956, the International Congress on Analytical Chemistry will meet in Lisbon (Portugal) under the guidance of the Analytical Section of the International Union of Theoretical and Applied Chemistry.

The work of the Congress will be divided into the following sections: 1) Microchemical Methods of Analysis, 2) Biological Methods, 3) Electrochemical Methods, 4) Optical Methods, 5) Radiochemical Methods, 6) Organic Complexes, 7) Statistical Interpretation of Results, 8) Adsorption and Partition Methods, 9) General Methods, 10) Standardization of Analytical Methods.

All reports presented at the Congress must be based on original investigations. General surveys are not recommended.

In order to assure that the work of the International Congress is of good quality, the Organizational Committee of the Congress believes it necessary that each country have its national organizations preliminarily select the reports that are presented.

Organizational Committee has been established by the Division of Chemical Science of the Academy of Sciences of the USSR to take charge of the participation of our scientists in the Congress.

At present a considerable number of papers have been examined and a preliminary list has been compiled of reports recommended for presentation at the Congress. These reports are the result of original researches of Soviet scientists in the most diverse branches of analytical chemistry.

More detailed information on the work of the Congress will be published as soon as it is available.

NOTICE

The Analytical Chemistry Committee at the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry of the Acad. Sci. USSR intends to convene, for October-November 1956, in Moscow, a conference on the application of organic reagents in analytical chemistry.

At the conference, reports on the above theme will be heard and considered; the chief topics are:

a) theory of action and selection of organic reagents;

b) application of organic reagents in inorganic analysis;

c) application of organic reagents in organic analysis;

The Analytical Chemistry Committee invites colleagues of all the Scientific-Research Institutes, Institutes of Higher Education and Factory Laboratories to participate in the conference.

Topics, theses and also requests for tickets of invitation should be sent to the Organizational Committee of the Conference before June 1, 1956.

The exact date of the conference will be announced at a future time.

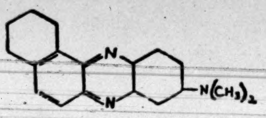
Organizational Committee of the Conference

NEW INDICATORS AVAILABLE

A NEW FLUORESCENT pH INDICATOR – DIMETHYLNAPHTHEIRODINE

(6-Dimethylamino-1,2-benzophenazine)

Structural formula:



A red-brown powder, soluble in alcohol.

Dimethylnaphtheirodine is used as a fluorescent indicator for detecting reactions, titration, and determination of pH of colored solutions. The change in fluorescence of indicator solutions in the ultraviolet from a lilac to orange occurs at pH 3.2-3.8.

For a detailed description see "Factory Labs" 20, 24 (1954).

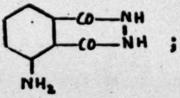
Dimethylnaphtheirodine is available at "Soyuzreaktivsbyt" in packets of 1g. For samples send to the following address : :

Moscow, Krivokolennyi Per. No. 12 "Soyuzreaktivsbyt"

A NEW CHEMILUMINESCENT pH INDICATOR – LUMINOL

(The hydrazide of 3-amino violetic acid)

Structural formula:



A yellow crystalline material.

Luminol is used for working (acid titration) with dark colored liquids. Luminol solutions glow in the dark at a pH greater than 8.

For a detailed description see Proc. Acad. Sci. USSR, 86, 115 (1952).

Luminol is available at "Soyuzreaktivsbyt". For samples send to the following address:

Moscow, Krivokolennyi Per. No. 12 "Soyuzreaktivsbyt".

ACADEMY OF SCIENCES USSR PRESS OFFICE "AKADEMKNIGA"

Published:

P. M. Lukyanov, History of Chemical Enterprises and Chemical Industry of Russia up to the End of the 19th Century. Edited by Acad. S. I. Volfkovich. Vol IV. (Div. of Chem. Sci., Acad. Sci. USSR. Institute of History of Natural Science and Technology). 1955. 821 pp.

Previously Published Books for Sale:

P. M. Lukyanov, History of Chemical Enterprises and Chemical Industry of Russia up to the End of the 19th Century. Edited by Acad. S. I. Volfkovich. Volume III. (Division of Chemical Sciences of Acad. Sci. USSR. Institute of History of Natural Science). 1951. 604 pp.

A. G. Bergman and N. P. Luzhnaya. Physico-Chemical Basis of Investigation and Utilization of Salt Deposits of the Chloride-Sulfate Type. (N. S. Kurnakov Institute of General and Inorganic Chemistry). 1951. 231 pp.

Historical Material on National Chemistry. Reports delivered at the sessions of the Leningrad Affiliate of the Committee on the History of Chemistry. (Div. Chem. Sci., Acad. Sci. USSR. Committee on History of Chemistry). 1954. 122 pp.

Acad. I. N. Nazarov, and L. D. Bergelson, Chemistry of Steroid Hormones. (N. D. Zelinsky Institute of Organic Chemistry). 1955. 752 pp.

Acad. A. P. Orekhov. Chemistry of Alkaloids. Second edition, corrected and supplemented by R. A. Konovalova, Dr. Chem. Sci. and A. A. Konovalova, Candidate Chem. Sci. (Div. Chem. Sci., Acad. Sci. USSR). 1955. 859 pp.

D. A. Petrov. Triple Systems. (N. S. Kurnakov Institute of General and Inorganic Chemistry). 1953. 310 pp.

State of the Theory of Chemical Structure in Organic Chemistry. Report of the Commission of the Division of Chemical Sciences of the Academy of Sciences USSR. 1954. 123 pp.

SPECTRUM ANALYSIS BY MEANS OF LINES LOCATED IN DIFFERENT REGIONS OF THE SPECTRUM – METHOD AND THEORETICAL BASIS

I. A. Kovalev

Branch of the All-Union Scientific Research and Construction Institute of Chemical Machine Construction

1. Modern methods of quantitative spectrum analysis are based on the formula

$$\Delta S = \gamma b \log c + \gamma \log a, \qquad (1)$$

which relate differences in blackening of spectrum lines (ΔS) on the photographic plate to the concentration (c) of a test element. This equation was derived by Lomakin [1], in 1930, by eliminating spectrum line intensity (I) from two forms of this equation:

$$S = \gamma \log I - \gamma j \qquad (2)$$

and

$$I = ac^b, \qquad (3)$$

where γ and j – are constants for a given photographic plate; a and b – are assumed to be constant for a standard method of igniting the test material, and for a definite concentration range. This formula is convenient in that it does not require measurement of the intensity of the spectrum radiation.

By constructing a graph within the coordinates ΔS – logarithm C, we get a straight line within the limits of normal blackening of the photographic plate. Thanks to the properties indicated, this formula lies at the basis of the modern development of quantitative spectrum analysis, and has become fundamental for a series of methods; in particular, for one of the most important methods – the so-called method of three standards.

Important conditions which must be satisfied if formula (1) is to be used are: small differences in the excitation potentials of the test pair of lines and near location of the reference lines on the photographic plate. In practice, difficulties often crop up in choosing suitable lines for analysis which lie close together; such difficulties limit the application of the spectrum method of anlaysis.

We have developed a spectrum method of analysis for such elements which do not have lines located close to each other. Let us assume that we have a pair of lines for two components which are located close to each other, and that they have similar excitation potentials. By means of this pair, as noted already, it is possible to carry out an analysis on the basis of formula (1).

Let us assume that there is a line for one of the components considered, which is absolutely identical with one of the lines of the pair indicated, but that it is located in another part of the spectrum. Despite the identity of the properties of the two lines (excitation potential and intensity) of the same element, their blackening will be different. The reasons for the differences in blackening are: change in contrast of the photographic plate for different wave lengths, and the heterogeneity of the photographic emulsion. If it should be possible to make a quantitative assessment of these factors, then, by multiplying the blackening of the line indicated by the corresponding factor, it should be possible to refer the modified blackening to the blackening of the line composing the pair of lines indicated above, and then carry out an analysis by means of formula (1). It is clear from this that if two lines of two components having similar values of the excitation potential are located in different parts of the spectrum, then, by multiplying the blackening of one of the lines by the corresponding coefficient, it is possible to use these lines for analysis on the basis of formula (1).

Determination of the Correction Coefficient

If we choose any spot on the photographic plate as a standard of homogeneity, then, in order to be able to refer the blackening of a line located in another spot on the plate to the given standard spot, it has to be multiplied by some coefficient of heterogeneity of the plate r. According to this we get the relation

$$S = rS', \tag{4}$$

in which the blackening S' of a line at a point is referred to the blackening S of the same line at the standard point.

In order to determine the correction factor for differences in contrast let us imagine a photographic plate with a homogenous emulsion, i.e. such that $r = 1$. Then, for the two lines of the same component, located in different parts of the spectrum, on the basis of equation (2), we get

$$S_2 = \gamma_2 \log I_2 - \gamma_2 j;\quad S_1 = \gamma_1 \log I_1 - \gamma_1 j$$

(In accordance with the fact that the value of j changes little with change in wave length as compared with γ, we shall assume that it is constant for a given photographic plate). From these last formulas, we get:

$$\log I_2 = \frac{S_2}{\gamma_2} + j;\ \log I_1 = \frac{S_1}{\gamma_1} + j.$$

Subtracting the second from the first, we get:

$$\log\frac{I_2}{I_1} = \frac{S_2}{\gamma_2} - \frac{S_1}{\gamma_1}.$$

Multiplying both parts by γ_2, we get:

$$\gamma_2 \log\frac{I_2}{I_1} = S_2 - \frac{\gamma_2}{\gamma_1}S_1. \tag{5}$$

The left hand side of this equation is the difference in blackening of the lines indicated, the contrast for which is equal to the contrast in the region of line 2. Accordingly, $S^0 = \frac{\gamma_2}{\gamma_1}S$ – is the blackening of the line with contrast γ_1, referred to the region with contrast γ_2. From which $\frac{\gamma_2}{\gamma_1}$ is the coefficient for converting the blackening of the line k to contrast γ_2. Taking into account the heterogeneity of the plate, and choosing as a standard of homogeneity that part of the plate emulsion where the line with blackening S_2 (for which $r = 1$) is located, and using equation (4) instead of equation (5), we get:

$$\gamma_2 \log\frac{I_2}{I_1} = S_2 - r\frac{\gamma_2}{\gamma_1}S_1', \tag{6}$$

where $S_1^0 = r\frac{\gamma_2}{\gamma_1}S'_1$ is the blackening of the line of component 1 on a heterogenous plate with contrast γ_1, referred to blackening on the part of line 2 with contrast γ_2

$$k = r\frac{\gamma_2}{\gamma_1} \tag{7}$$

is the correction coefficient for blackening required for calculating the heterogeneity of the plate emulsion, and the difference in contrast. In the case where the lines are located side by side, then $r = 1$; $\gamma_1 = \gamma_2$: $k = 1$, and formula (6) reduces to

$$\Delta S = \gamma \log \frac{I_2}{I_1}\,,$$

which agrees with the conditions obtaining in Lomakin's equation (1).

Derivation of an Equation Relating Spectrum Line Blackening to Concentration

Let us write equation (3) for two test components:

$$I_2 = a_2 c_2^{b_2}, \; I_1 = a_1 c_1^{b_1}. \tag{8}$$

If the lines have near values for the excitation potential, while the intensities and concentrations of the atoms of the given elements in the arc are not high, then b_1 and b_2 may be assumed to be equal to each other [2]. Dividing the first equation in (8) by the second and taking logarithms, we get, successively:

$$\frac{I_2}{I_1} = \frac{a_2}{a_1}\left(\frac{c_2}{c_1}\right)^b; \; \log \frac{I_2}{I_1} = b \log \frac{c_2}{c_1} + \log \frac{a_2}{a_1}.$$

Substitution of the last equation in equation (6) gives the required formula:

$$S_2 - kS_1' = \gamma_2 b \log \frac{c_2}{c_1} + \gamma_2 \log \frac{a_2}{a_1}. \tag{9}$$

This is the formula which must be used for analysis by the three standards method in cases where the analytical lines are located in different parts of the spectrum; it is a more general equation than that of Lomakin which is a special case of it. Since relative concentrations are used, it is suitable for use both at low and high concentrations. If we put $\gamma_1 = \gamma_2$; $r = 1$; $k = 1$; $c_1 = 1$; $\frac{a_2}{a_1} = a$, then formula (9) reduces to Lomakin's formula (1).

Application of the Method

The equation just derived (9) has been used for determination of the ratio of sodium to potassium concentration in aqueous solutions when these elements are present as the sulfates and chlorides. Determination of this ratio is usually necessary for resolving the sum of the alkalis. For the given components, formula (9) is written in the form:

$$S_{Na}' - kS_K' = \gamma_2 b \log \frac{c_{Na}}{c_K} + \gamma_2 \log \frac{a_{Na}}{a_K}. \tag{9'}$$

8 mm polished copper electrodes were used; the lower electrode was planar, while the upper was hemispherical. Before carrying out an analysis, the washed and dried operating parts of the electrodes were cleaned with a pure file of oxide; the electrodes were then moistened by immersion in test solution and dried on a specially constructed hot plate (Fig. 1).

Spectra were excited with an A.C arc; the current used for chloride solutions was 5 A, while it was 6 A for sulfates. Inter electrode distance was 2 mm. Spectra were photographed on a diapositive photographic plate with a sensitivity of 3-4° on the K and D scale, by means of an ISP-22 spectrograph.

The method just described for introducing the test material into the arc, in view of the identity of properties of the similar salts of sodium and potassium, and the absence of fractional evaporation, ensured that sodium and potassium atoms entered the inter electrode space in the same ratio as they were found in the test material. Analysis was carried out using the lines Na λ 3302.3 A and K λ 4044.1 A. The correction factor "K" was determined by using the lines of the electrodes Cu_2 λ 3290.5 A and Cu_1' λ 4022.7 A.

The fundamental properties of the lines used are given in Table 1.

According to equation (7), in order to determine K, it is necessary to determine γ_1, γ_2, and r.

To determine γ_1 and γ_2 it is sufficient to photograph the spectrum of the copper electrodes on the plate through a graduated attenuator, under the conditions used during an analysis. After constructing the blackening curves for the two copper lines located near the lines Na λ 3302.3 A and K λ 4044.1 A, γ_1 and γ_2 are calculated.

TABLE 1

Properties of the analytical lines [3]

Line designation	Extent of ionization of the atom	Intensity	Excitation potential eV
K λ 4044.1 A	Neutral state	800	3.06
Cu_1 λ 4022.7 A	• •		6.87
Na λ 3302.3 A	• •	600	3.75
Cu_2 λ 3290.5 A	• •		8.84

Determination of the correction factor for heterogeneity is somewhat more complex, and accordingly, requires more detailed consideration.

On the basis of the definition in formula (4) we write:

$$r\frac{S_k}{S'_k} = \frac{S_{Cu_1}}{S'_{Cu_1}}.$$

According to the equation, $\Delta S_{Cu_2,\,Cu_1} = S_{Cu_2} - S_{Cu_1}$ we get:

$$r = \frac{S_{Cu_2} - \Delta S_{Cu_2,\,Cu_1}}{S'_{Cu_1}}. \qquad (10)$$

Considering the terms of this formula, we see that the terms S'_{Cu_1} and S_{Cu_2} ($= S'_{Cu_2}$) can be determined directly by measuring the blackening of the copper lines chosen, which are near the analytical lines Na 3302.3 A and K 4044.1 A. Nevertheless, it is impossible to determine $\Delta S_{Cu_2,\,Cu_1}$ in practice, since it is a difference between two lines located in a plate with a homogenous emulsion. We used the following method to determine $\Delta S_{Cu_2,\,Cu_1}$.

Alongside the analytical lines Na λ 3302.3 A and K 4044.3 A, the two copper lines Cu_2 λ 3290.5 A and Cu_1 λ 4022.7 A were also photometrically measured. For each spectrogram the difference in their blackening was determined; these values were then measured for all the spectrograms on a given plate. This mean value was also accepted as the difference in blackening of the lines of a homogenous plate, which, for a large number of spectrograms on a plate, was satisfactorily determined. The correction factor r was then determined for each spectrogram by means of formula (10).

Equation (9) derived for lines located at any distance, satisfies all the conditions which Lomakin's equation (1) satisfies for lines located near each other. Thanks to this, all methods based on equation (1) are also applicable to equation (9). As an illustration of the applicability of equation (9), two graphs are given which depict the results of two series of photographs on two plates.

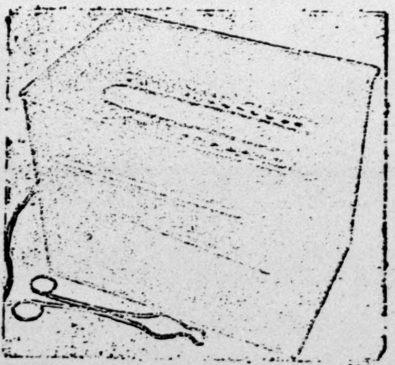


Fig. 1. Electric hot plate for drying electrodes.

On the graphs (Fig. 2) are shown the distribution of points relating the ratio of sodium and potassium concentrations to differences in blackening. Curves depicted by complete lines are those in which the heterogeneity of the plate and the differences in contrast are taken into account by introduction of correction k; points connected by the dotted line, correspond to differences in blackening when no account has been made of the heterogeneity of the plate. It is clear from these graphs, that points, in which the individual heterogeneity of the plate is taken into account, lie on a straight line, while points in which no account has been taken of the heterogeneity, do not lie on a straight line.

During a study of the applicability of the method to the analysis of aqueous solutions of the chlorides and sulfates of sodium and potassium, it was established that the method gives satisfactory results for concentrations of from 0.006 g/cm³ for potassium, and 0.0005 g/cm³ for sodium, under the operating conditions for spectrographing described. The ratios of component concentrations which can be analyzed by the method under discussion lies within the limits

$$\frac{c_{Na}}{c_K} \text{ from } \frac{1}{40} \text{ to } \frac{1}{1}.$$

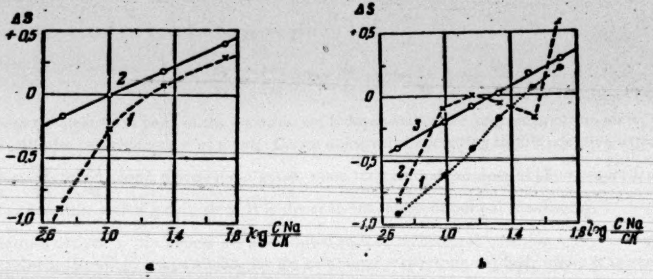


Fig. 2. Arrangement of points on calibration curves. a: 1) without correction; 2) with correction k. b: negative logarithms are given on the abscissa. 1) with correction r; 2) without correction; 3) with correction k.

TABLE 2

Results of spectrographic determination of alkali metals in solution

Experiment No.	Actual content in %		Found		Relative error in %	
	Na	K	Na	K	Na	K
1	0.9254	1.3884	0.9694	1.3445	+ 4.7	— 3.2
2	0.9254	1.3884	0.9431	1.3708	+ 1.9	— 1.3
3	1.0450	1.2291	1.0534	1.2206	+ 0.8	+ 0.8
4	0.8328	1.3860	0.8163	1.4025	— 3.2	+ 1.8
5	0.6345	1.5840	0.6473	1.5712	+ 2.1	— 0.8
6	0.2776	1.9403	0.2859	1.9320	+ 3.0	— 0.4
7	0.2467	1.9712	0.2447	1.9733	+ 0.8	+ 0.1
8	0.2221	1.9957	0.2447	1.9731	+10.2	— 1.1
9	0.1586	2.0593	0.1492	2.0687	— 5.9	+ 4.6
10	0.2220	1.9957	0.1933	2.0244	—12.9	+ 1.4
11	0.1480	1.8480	0.1545	1.8415	+ 3.7	— 0.4
12	0.2776	1.9404	0.2928	1.9252	+ 5.5	— 0.8
13	0.1306	2.0872	0.1148	2.1086	—12.1	+ 1.0
14	0.5552	1.6320	0.5219	1.6565	— 6.0	+ 3.9
15	0.3333	1.6667	0.3456	1.6544	+ 3.7	— 1.0
16	0.1818	1.8182	0.1781	1.8219	— 2.1	+ 0.2
			Mean error		4,9	1,4

Within these limits, under the operating conditions described, blackening of analytical lines is within the limits of normal blackening. Table 2 contains results on the analysis of solutions of sodium and potassium sulfates when the method described was used. The solutions were specially prepared for checking the method, by the analytical laboratory of our Institute.

Construction of a Permanent Graph

By writing equation (9) in the form

$$S'_2 - \frac{\gamma_2}{\gamma_1} r S'_1 = \gamma_2 \log \frac{I_2}{I_1} = \gamma_2 b \log \frac{c_2}{c_1} + \gamma_2 \log \frac{a_2}{a_1}$$

and dividing all the parts of the equation by γ_2 we get:

$$\frac{S_2}{\gamma_2} - \frac{rS_1}{\gamma_1} = \log \frac{I_2}{I_1} = b \log \frac{c_2}{c_1} + \log \frac{a_2}{a_1}.$$

Since both the right hand parts of the equation are independent of the properties of the plate, then the left hand side will also be independent of them. Curves constructed according to this equation within the coordinates $\frac{S_2}{\gamma_1} - \frac{rS_1}{\gamma_1}, \log \frac{c_2}{c_1}$ form a permanent graph, since they are independent of plate properties; three points are sufficient to construct such a graph, since it is linear in the region of normal blackening.

The relations derived in this article are not limited to spectrochemical emission analysis; they can be used for molecular spectroscopy, in particular for the combination spectrum method, where it is necessary to carry out photometric measurements on lines at large distances from each other.

In conclusion, the author wishes to thank M. P. Ermakova who took part in preparing standards.

SUMMARY

1. A spectrum method of analysis has been worked out which is based on lines located in different parts of the spectrum.

2. A formula has been derived for the case under consideration, which relates line blackening to test material concentration.

3. The method developed is applicable to the determination of the ratio of sodium and potassium, using the lines Na λ 3302.3 A and K λ 4044.1 A.

4. Recommendations are made re the application of the formulas derived to other spectral methods of study.

Received December 13, 1954

LITERATURE CITED

[1] B. A. Lomakin, Z. anorg. allg. Chem., 187, 1, 75 (1930).

[2] S. L. Mandelshtam, "Introduction to Spectrum Analysis", United State Press, Moscow-Leningrad, 1946, p. 43.

[3] A. N. Zaidel. V. K. Prokofiev, and S. M. Raisky, "Tables of Spectrum Lines", Moscow-Leningrad, State Sci. Tech. Lit. Press (1952).

EFFECT OF BULK COMPOSITION ON THE ENTRY OF INDIVIDUAL TEST ELEMENTS INTO THE ARC FLAME

T. F. Borovik-Romanova

THE V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, Moscow

The effect of the bulk composition of test material on spectrum line intensity, which we have studied several times [1, 2], is a factor which complicates fullfilment of accurate quantitative analysis. As Mandelshtam has shown [3], one of the casues of these phenomena, may be changes in arc flame temperature.

On the other hand, of no little importance from the point of view of quantitative spectrum analysis, is the character of the evaporation processes of test material components, and their entry into the arc flame.

During evaporation of an ore from the cavity of a carbon electrode, fractional evaporation of individual test elements may occur; this is a factor which is important to bear in mind when carrying out quantitative analysis.

A. K. Rusanov [4, 5], studied evaporation of various elements and their compounds, as well as that of various ore samples, from the cavity of a carbon electrode into a D.C. arc. On the basis of his results, he compiled a volatility series for the elements and their compounds.

In the work described in the present article, a study was made, of how the order in which individual elements enter the arc flame varies during evaporation of various alumino-silicates from the cavity of a carbon electrode in a D.C. arc; the test materials were alumino-silicates differing in composition, such as granite, mica, basalt, clay, etc. In addition, the effect of addition of various materials to the test material, on the order of entry of individual elements into the arc flame was studied.

A D.C. arc was used which was supplied at 250 V from a mercury rectifier; the current was kept at 8 A. Carbon rods 6 mm in diameter were used as electrodes; the lower electrode had a cavity 6 mm deep and 3.5 mm in diameter; sample weight was 0.03 g; interelectrode distance 4 mm. The lower electrode served as the anode. Spectrograms were photographed on a moving plate. The plates were moved continuously at a speed of 5 mm/minute, or at 30 second intervals, sometimes — 60 seconds. A three lens system of illumination with an intermediate image was used. The middle part of the arc flame was projected. Samples of granite, mica, basalt, and clay, whose main components are SiO_2, Al_2O_3, Fe_2O_3, MgO, Na_2O and K_2O, were studied. Blackening of the lines of the principal elements of the test materials, Al, Si, Mg and Na was measured on the spectrograms obtained by means of an MF-2 microphotometer.

The graphs obtained are shown in Fig. 1; it can be seen from these that test elements proceed into the arc flame in the same order, in the case of mica and granite. The intensity of silicon lines, which is appreciable in the first minute, increases to its maximum value in the fourth minute and becomes very weak toward the end of the sixth minute. The intensity of Al and Mg lines, which is very insignificant in the first minute, rapidly increases during the second and third minutes, and attains a maximum toward the end of the fourth minute; by the end of the sixth minute, Al and Mg lines are no longer visible. The intensity of the sodium line starts to increase in the second minute, and attains its maximum in the third minute; all the sodium has evaporated from the test sample by the end of the fourth minute.

Differences in the evaporation of sodium and silicon are observed in the case of basalt. The sodium lines are already intense during the first minute of arc burning, and gradually weaken toward the end of the fourth minute. The entry of silicon into the arc flame from basalt samples is more uniform.

Large differences are observed in the order of entry of individual test elements in the case of clay. The intensity of aluminum, silicon, and magnesium lines respectively, attains a maximum in the second minute; subsequently, with small variations, it remains almost the same up to the fourth minute, when it rapidly decreases. Sodium line intensity is highest during the first minute, it subsequently weakens uniformly; sodium in clays evaporates toward the end of the fourth minute of arc burning.

It should be noted that the character of the evaporation of test material is more stable, when the electrodes and test material are given a preliminary heating with the current for 15 seconds.

The nature of the evaporation of test materials can be modified to a considerable extent by mixing various materials with test samples.

We studied the effect of addition of NaCl, Na_2CO_3, and carbon powder on the evaporation of granite; these additives were mixed with test material in the ratio of 1:1; we also investigated the effect of simultaneous addition of carbon powder + sodium chloride, and of carbon powder + nickel oxide. Sodium has a low ionization potential, and its compounds are often used for stabilizing arc temperature. The results obtained are shown in Fig. 2.

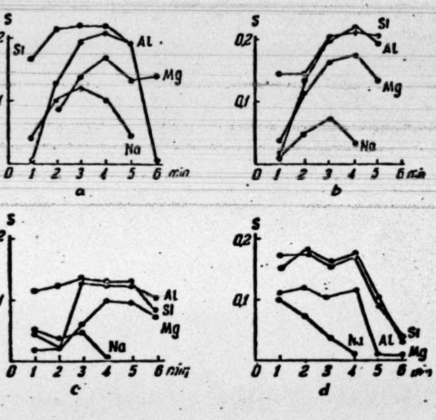


Fig. 1. Evaporation curves from the cavity of a carbon electrode for granite (a); mica (b); basalt (c); and clay (d).

These graphs show that on addition of NaCl to granite in the ratio of 1:1, evaporation of such elements as Si, Al, and Mg is delayed, while the entry of these elements into the arc flame only starts intensively when almost all the sodium has evaporated — this occurs during the fourth minute. Entry of silicon during the first and second minutes is insignificant; silicon lines only become more intense during the third minute, after which silicon line intensity increases rapidly, and reaches its maximum during the fifth minute; it drops rapidly after this. The intensity of Al and Mg lines is also a maximum during the fifth minute.

A similar retardation in evaporation of Si, Al, and Mg in the case of granite test samples was also observed, when sodium chloride was not added to the test sample, but was introduced into the upper electrode. In these cases, the upper electrode consisted of a rod 6 mm in diameter and 2.5 cm long; a cavity 3.5 mm in diameter was made in the rod; the depth was such that the bottom which was left was only 2 mm thick; an opening 0.8 mm in diameter was drilled in this. Sodium chloride was strewn in the electrode, after which the electrode was covered with a small carbon rod. The electrode was fitted in a clamp in such a way that the bottom opening was turned toward the lower electrode*. After firing the arc, sodium chloride starts to fall into the arc flame through the opening. During the initial period, when this method is used, while the entry of sodium is insignificant, Si, Al, and Mg pass into the arc flame in the same way as for granite to which no sodium salt has been added, but, even after a minute, there is strong weakening of the Si, Al, and Mg lines; subsequently, the character of the entry of the elements indicated into the arc flame is similar to that which occurs when sodium chloride has been mixed in with test material.

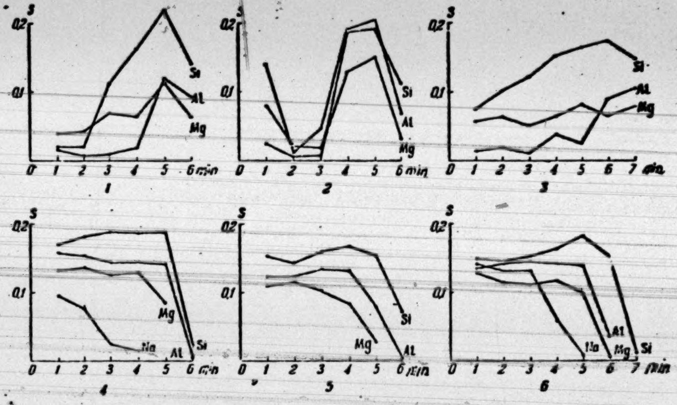


Fig. 2. Evaporation curves from the cavity of a carbon electrode for granite to which various materials have been added.
1) Granite + NaCl in the ratio 1: 1; 2) granite, NaCl introduced into the upper electrode; 3) granite + Na_2CO_3 (1: 1); 4) granite + carbon powder (1: 1); 5) granite + carbon powder + + nickel oxide (1: 1: 4); 6) granite + carbon powder + NaCl (1: 1: 4).

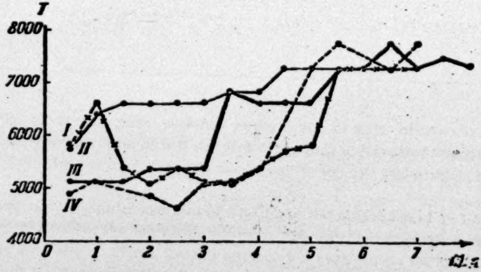


Fig. 3. Changes in temperature:
I) Granite; II) granite + carbon powder; III) granite + carbon powder + NaCl; IV) granite + NaCl.

---

* Yu. I. Belyaev used an electrode of this type for analyzing granites.

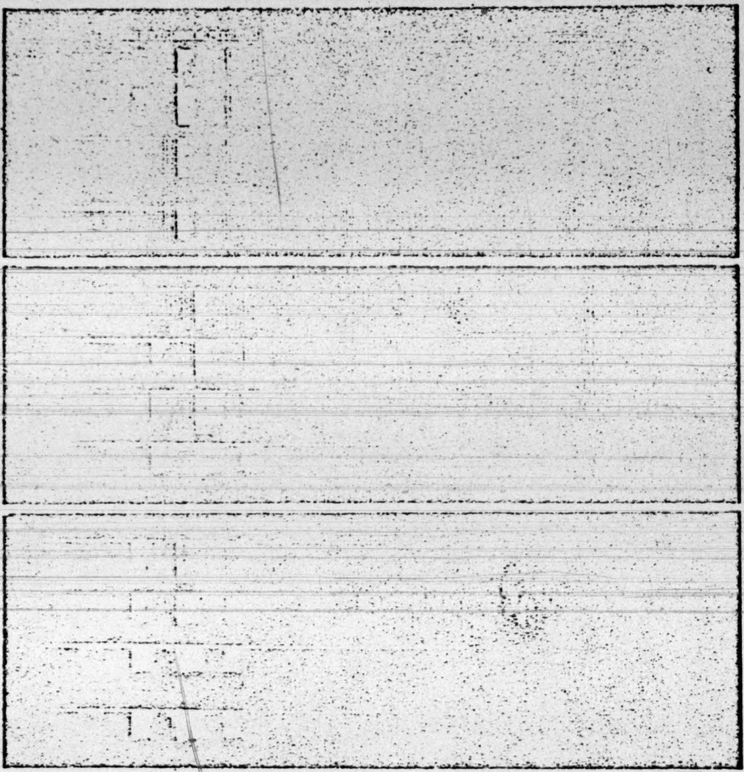


Fig. 4. Spectrograms obtained in the course of a six minute exposure on a plate which was moved during evaporation of test samples of granite; a decreased stigmatic image of the arc was projected on the slit. In each case the anode was on top and the cathode below.

Addition to granite samples of Na_2CO_3 in the proportion of 1:1 also inhibits evaporation of the principal elements of granite; the inhibiting effect is, however, not so marked as when sodium chloride is used. In this case, the intensity of silicon lines is appreciable even during the first minute, and gradually increases up to the sixth minute, after which it starts to drop; the intensity of aluminum lines is highest in the seventh minute. Magnesium line intensity remains almost a constant, increasing to an insignificant extent toward the end of the exposure.

Addition to granite samples of carbon powder leads to a sharp change in the nature of the entry of the principal elements into the arc flame, and there is observed a more uniform evaporation of all these elements. Al, Si, Mg, and Na line intensity is already appreciable during the first minute, and remains practically constant up to the fifth minute, except in the case of the sodium line whose intensity gradually increases toward the end of the fourth minute.

When carbon powder and sodium chloride are added simultaneously to granite in the proportion of 1:1:1, the nature of evaporation is similar to that observed when test samples are mixed with carbon powder alone, exept that in this case evaporation of all the test material takes longer (Fig. 2). When granite samples are mixed with carbon powder and nickel oxide in the ratio 1 : 1 : 4, the principal elements of the test material— Si, Al, and Mg begin to pass into the arc flame at the same time and at a uniform rate (Fig. 2).

Similar results were obtained on addition of sodium chloride, carbon powder, and carbon powder + NaCl, respectively, to basalt samples. During our investigation, attention was paid to changes in temperature of the arc column when additives were used. Approximate measurements of temperature were made by means of a voltmeter as suggested by Rusanov [1]. To convert voltmeter readings to temperature, we used Semenova's results [6], since our operating conditions were similar to hers.

In Fig. 3 are given graphs illustrating changes in temperature of the arc flame during exposure, on evaporating test samples of granite, granite + carbon powder, granite + NaCl, and granite + carbon powder + + NaCl, respectively, from the electrode cavity.

On evaporating granite samples from the electrode cavity, there was observed, during the second minute of exposure, a drop in arc flame temperature to ca. 5000° K; this temperature, with certain variations, was maintained up to the fourth minute, when it started to increase. When all test material had evaporated, temperature rose to 7400° K.

On evaporating granite with carbon powder, the temperature rose during the second minute of exposure to ca. 6600° K, and remained practically constant to the end of the fourth minute, when it rose to 7400° K. On evaporating granite + NaCl, the flame temperature was very low ~4800° K; the temperature started to rise during the fourth minute of exposure when all the sodium evaporated.

When granite mixed with carbon powder and sodium chloride was evaporated, the temperature during the first three minutes was ca. 5000-5200° K, after which it rose to a temperature which corresponded to that when test samples were mixed with carbon powder alone (ca. 6600° K); after evaporation of all the sample, the temperature rose to 7400° K in this case also. It is worthy of note that the temperature remained most constant when carbon powder was added to the test granite.

Photographs were also taken of granite samples by projection of a diminished stigmatic image on the spectrograph slit. Spectrograms of this type allow one to observe the distribution of spectrum line intensity throughout the whole extent of the arc flame during exposure. In these cases, we obtained series of spectrograms taken one after the other with exposures of 30 seconds, for each sample. On completion of each exposure, the casette was shifted forward 9 mm. When the casette was being moved forward, the arc was interrupted and started off again when the next exposure was to be taken, by means of a carbon rod. Complete evaoporation of one test sample took 6 minutes; this meant that 12 spectrograms could be obtained (Fig. 4). From these spectrograms it is clear that during the first minute, only a small number of weak lines appear. At the beginning of the second minute, the intensity of most of the lines strengthens appreciably, lines near the anode are observed to be stronger. Toward the end of the second minute, the lines become intense along their whole length, being slightly more intense near the anode; intensification also occurs near the cathode. During the third minute, intensification of the lines near the anode starts to weaken, while, at the same time, the parts of the lines near the cathode become stronger. During the fourth minute, an appreciable weakening of line intensity is observed near the anode and the middle; intensification of the parts of the lines in the region of the cathode becomes more noticeable. At the end of the fourth minute, and also during the fifth and sixth minutes, the parts of the lines near the middle and the anode disappear, and then there remains only a band of short lines near the cathode. These photographs show graphically how the nature of the distribution of line intensity varies with time, along the length of the arc flame. It should be noted that right at the beginning of exposure, when the lines start to intensify near the cathode, lines are observed which do not appear in other parts of the flame; these lines are characterized by high excitation potentials, e.g. the lines Mg 2790 A (excitation potential 8.86 eV) and the line Mg 2967.2 A (excitation potential 14.2 eV).

These photographs show that the intensity of the same line of a test element is not uniform along the arc flame, and that the intensity changes during exposure; accordingly, during quantitative analysis it is very important that the slit should always be illuminated by a strictly defined part of the arc flame.

The present study of the effect of bulk composition on the dynamics of evaporation of Si, Al, Mg, and Na had as its aim, establishing conditions under which the test elements proceed into the arc flame as uniformly as possible; the application of such conditions may be useful for carrying out quantitative analysis.

In conclusion, I should like to thank Academician A. P. Vinogradov, and S. A. Borovik for their valuable advice and help in this work.

SUMMARY

1. It has been found that the entry of Al, Si, Mg, and Na into an arc flame from a carbon electrode differs in the case of granite, basalt, and clays.

2. Addition of various materials to test granite and basalt affects the nature of evaporation of the test:

a) addition of sodium chloride inhibits evaporation of the principal test elements;

b) addition of Na_2CO_3 also inhibits evaporation of Al, Si, Mg but to a significantly lesser extent;

c) addition of carbon powder, or of carbon powder + sodium chloride, or carbon powder + nickel oxide, permits uniform evaporation of sample.

3. Arc flame temperature changes during passage of test elements into the flame, with changes in bulk composition; the temperature remains most stable when carbon powder is added to test material.

Received February 2, 1955

LITERATURE CITED

[1] S. A. Borovik and T. F. Borovik-Romanova, Proc. Acad. Sci., 15, 543 (1937).

[2] S. A. Borovik and T. F. Borovik-Romanova, J. Anal. Chem., 1, 25 (1946).

[3] S. L. Mandelshtam, Proc. Acad. Sci., 18, 559 (1938).

[4] A. K. Rusanov, "Spectrum Analysis of Ores and Minerals", 1948.

[5] A. K. Rusanov, Bull. Acad. Sci. USSR, Phys. Ser. No. 2-3, 235 (1941).

[6] O. P. Semenova, Proc. Acad. Sci., 51, 683 (1946).

SPECTROGRAPHIC DETERMINATION OF SILICON AND LEAD IN POWDER USED FOR THE PRODUCTION OF SYNTHETIC CORUNDUM

O. P. Malkova and N. K. Rudnevsky

Scientific Research Institute of Chemistry affiliated with Gorky University

The object of the work described here was to develop a spectrographic method for determining silicon and lead in aluminum oxide powder, used for corundum production. The following methods of introducing the powder into an arc discharge were tried out: moving copper and carbon discs [1], and evaporation from the opening in a carbon electrode. Tests showd that on evaoprating powder from a copper late electrode, the intensity of silicon lines, at concentrations of silicon in the powder less than 0.01%, was insignificant; on evaporation from the opening in a carbon electrode, reproducibility of results was low. A significant increase in blackening of the silicon lines, even for comparatively short exposures, was observed on substituting the copper electrode by a carbon one. For a content of $3.10^{-3}\%$ of silicon in the powder, and an exposure of 60 seconds on plates with a sensitivity of 6° H. and D blackening of the silicon line Si 2516.12 A amounted to 1.5. Similar blackening was obtained for the lines Pb 2614.18 A and Pb 2802.0 A. The lower electrode was prepared in the shape of a flat carbon plate 7-12 cm long. A groove 4 mm long and 0.5 mm deep was made in the middle of the plate. Flanges on the groove prevented creep of test material from the plate during arc operation. The carbon plate was made from spectrographically pure carbon on a small lathe specially designed for the job. In order to remove any silicon which might be present as an impurity in the carbon electrodes, the latter were subjected to a preliminary heat treatment. Burning the silicon out from the groove in the lower electrode was particularly difficult. It was established that in order to get rid of silicon from the groove in the carbon plates 10 cms long, it was necessary to carry out combustion for 4 minutes using a current of 9 A for heating. Combustion was carried out by uniform movement of the arc flame along one flange and then up the other (Fig. 1). After this heat treatment, test samples were strewn on the carbon plate and made level with the edges of the groove. A carbon rod 4.5 cm long served as the upper electrode. The end of the electrode was ground flat and submitted to combustion together with the carbon plate. While the spectra were being photographed, the lower electrode + test sample was moved uniformly with respect to the upper electrode by means of a little motor. The arc flame was directed along the flange of the plate located near the slit of the apparatus. Inter-electrode distance was 2.5 mm; the rate at which the lower electrode was moved was 0.16 cm/sec. An A.C. arc operating on a current of 6 A was used as source. Spectra were photographed with an ISP-22 spectrograph using an exposure time of 40 seconds. An NIKFI* plate of sensitivity 6° H. and D. was used. A two lens attenuator was fitted in front of the spectrograph slit. Blackening of test element lines was determined on the basis of the non-cleared, and the reference lines on the basis of the cleared stages of the attenuator. The lines were photometrically measured by means of an MF-2 microphotometer. Determination of silicon in the powder at silicon concentrations not exceeding $10^{-2}\%$ was carried out using the pair of lines Si 2516.12 A - Al 2652.49 A. At higher silicon concentrations, it was found to be more convenient to use the less intense silicon line Si I 2524.12 A. The following pairs of lines were used for lead determinations: Pb 2614.18 A-Al 2652.49 A and Pb 2802.0 A-Al 2652.49A. These pairs

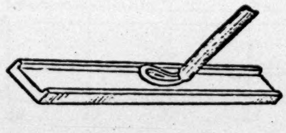


Fig. 1. Preliminary heat treatment of the carbon plate to get rid of silicon.

---

* Scientific Research Institute for Motion Pictures and Photography.

of lines have a greater concentration sensitivity than the pair Pb 2833.07 A-Al 2652.49 A (Fig. 6). Standards were prepared by adding known amounts of lead and silicon to the powder. Lead was added as the nitrate; this was subsequently converted into oxide by calcining the standard at 400°. Silicon was introduced as a solution of sodium silicate. It is known that introduction of alkali metal salts leads to a drop in discharge temperature. In this connection therefore, the necessity arose of studying the effect of sodium salts on the relative intensity of the lines. Results of this series of tests are given graphically in Fig. 2, where the dotted line represents the value of the relative intensities of the lines in the absence of sodium salts. This spectrographic method of determining silicon and lead was worked out for contents of these elements of not more than 0.05%. For silicon concentrations of this order, the concentration of sodium introduced as the salt $Na_2SiO_3 \cdot 9H_2O$ amounts to ca. 0.1%. It is evident from Fig. 2 that addition of sodium in amounts of 0.1%, has practically no effect on the relative intensity of the analytical pair of lines of silicon and lead. Silicon is present in the powder mainly as SiO_2, while in the standards it is in the form of the salt Na_2SiO_3. In order to clarify the effect of the molecular state of silicon on the relative intensity of the analytical pairs of lines, photographs were taken of the spectra of powders in which the silicon, while being of the same concentration in each case, was in the form of SiO_2 in some and as Na_2SiO_3 in others. In the first case, the mean value of the logarithm of the relative intensity of the pair of lines Si 2516.12 A-Al 2652.49 A was 0.53, while in the second it was 0.50. From these results it follows that, in our case, the type of molecular compound has practically no effect on the relative intensity of the silicon lines. It was thus demonstrated that it is possible to use sodium silicate for preparing standards. A study was next made of the mutual effect of silicon and lead on the relative intensity of the analytical pairs of lines. The results obtained are represented graphically in Fig. 3. The dotted line represents the value of the relative intensity of the lines when no lead or silicon is present. It is clear from these graphs that no mutual effect of lead and silicon on the relative intensity of the lines of their analytical pairs is observed. We noted that the aluminum oxide is hygroscopic, changes in weight of the powder after calcining at 400° was therefore studied. It was found that the weight of powder decreases by about 5% during calcining. After 24 hours the weight of powder again increases, and becomes approximately constant. On keeping the powder for a further period in air, variations in weight of the powder amounted to ca. 0.3% (Fig. 4). In addition to this a study was made of the change in relative intensity of the silicon and lead lines with time after calcining the powders (Fig. 5). This Fig. 5 is a plot of the difference in the logarithms of the relative intensity of the lines obtained on photographing the spectra of powder calcined at 400° (log R_2) and that of uncalcined powder (log R_1). Point a on the graph relates to a powder whose spectrum was photographed three months after calcining. It follows from Fig. 5 that before photographing the spectra of standards, it is expedient to keep them in air for 24 hours after calcining, since, at the end of this

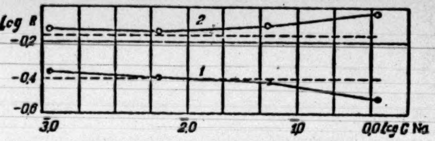


Fig. 2. Relation between relative intensity of the lines and the amount of NaCl added to the powder:
1) Si 2516.12A-Al 2652.49 A, 2) Pb 2614.18 A-Al 2652.49 A.

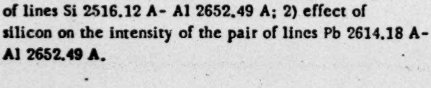


Fig. 3. Mutual effect of lead and silicon in the powder on the intensity of their lines.
1) Effect of lead (as PbO) on the intensity of the pair of lines Si 2516.12 A- Al 2652.49 A; 2) effect of silicon on the intensity of the pair of lines Pb 2614.18 A-Al 2652.49 A.

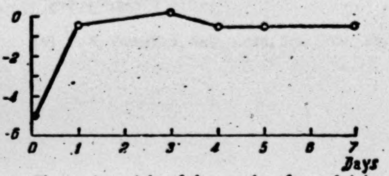


Fig. 4. Change in weight of the powder after calcining at 400°.

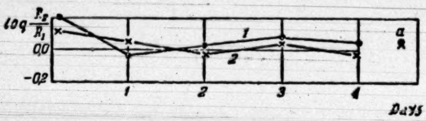


Fig. 5. Change in relative intensity of the lines after calcining the powder at 400°.
1) Si 2516.12 A-Al 2652.49A; 2) Pb 2614.18 A-Al 2652.49 A.

TABLE 1

Standards	Lead concentration Pb in %	Si concentration in %	
		By the approximation method	By Prokofiev's method of additions
Standard I	$2.9 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$
Standard II	$2.8 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	$2.2 \cdot 10^{-3}$

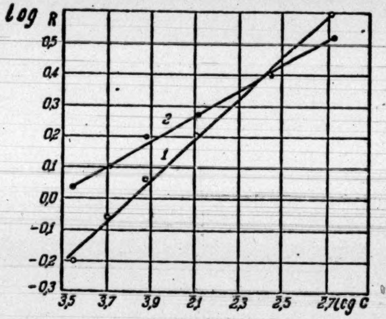


Fig. 6. Calibration curve for lead constructed for various pairs of analytical lines:
1) Pb 2614.18 A-Al 2652.49A; 2) Pb 2833.07A-Al 2652.49 A.

period, variations in the relative intensity of the lines is least. Determination of unknown concentrations of lead and silicon in powders used for preparing standards, was carried out by the method of graphical approximation [2, 3]. Determination of silicon was also carried out by Prokofiev's method of additives [4], since the value of coefficient b for the pair Si 2516.12 A-Al 2652.49 A was found to be approximately one, while for lead on the basis of the pair Pb 2614.18 A-Al 2652.49 A the value of b varied from 0.7-0.8. We used standards containing only lead, or silicon, respectively (standard I), as well as standards containing both lead and silicon (standard II). Table 1 contains mean results for five determinations of silicon and lead in the same test powder, on the basis of the standards prepared. Series of analysis should be carried out by the three standards method, using standards containing both lead and silicon. Figure 6 illustrates the calibration curves for determining lead in powders. The probable error for silicon determination using the pair of lines Si 2516.12 A-Al 2652.49 A is equal to ± 11%, while for lead, using the pair of lines Pb 2614.18-Al 2652.49 A the error is ± 12%. Calculation of the probable error was made on the basis of 50 spectrograms.

SUMMARY

A spectrographic method has been developed for determining lead and silicon in aluminum oxide used for the production of synthetic corundum.

Received December 10, 1954

LITERATURE CITED

[1] N. K. Rudnevsky and O. P. Malkova, Factory Labs., 18, 11 (1952).

[2] N. K. Rudnevsky, P. N. Ivagina and P. N. Ivagin, Bull. Acad. Sci. USSR, Ser. Phys. 14, No. 5 (1950).

[3] V. K. Prokofiev, "Photographic Method for Quantitative Spectrographic Analysis of Metals and Alloys" Part II, GITTL, 1951.

[4] V. K. Prokofiev, Bull. Acad. Sci. USSR, Phys. Ser. 14, (State Tech.-Theor. Lit. Press) No. 5(1950).

HIGH FREQUENCY TITRATION

III. ANALYTICAL CONTROL IN THE PRODUCTION OF PLASTICS

B. P. Ershov, V. L. Pokrovskaya, V. A. Zarinsky, and D. I. Koshkin

Institute of Plastic Materials of the Ministry of Chemical Industry, and the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow

Despite the large number of published articles on high frequency titration, there are practically no examples of the application of this method to production control in the periodical literature; such examples would serve as proof of the advantages which this method has over others. Nevertheless, the characteristic feature of a high frequency current of passing through dielectrics emulsified in an electrolyte, which we have pointed out previously [1], opens up direct possibilities of titrating production solutions. This possibility was demonstrated by our experiments on the determination of acids and alkalis in dark colored solutions of synthetic resins and plasticisers. The present article is devoted to further development of production control methods (by means of high frequency current-H. F. current) for materials used in plastics production.

1. Acid-Base Titration

We assembled an apparatus according to the scheme suggested by the Institute of Geochemistry of the USSR Academy of Sciences, using a 36 megacycle generator [1]. The titration cell used in the present instance differed somewhat in constructional details from that described previously; it was constructed in such a way that it could be fitted on to details mounted on the outer surface of the beaker (casing, choking coil, detector).

When the apparatus had been assembed it was checked by titrating solutions of NaOH and HCl of different but known concentrations. The volume of alkali pipeted into the titration beaker was made up to 50 ml, so that the level of solution was higher than the upper edge of the electrode. This was an essential precaution in order to eliminate the effect of volume changes on micro-ammeter readings (the so-called "volume effect").

The number of ml of hydrochloric acid added from a buret and micro-ammeter readings were tabulated, and plotted graphically, the micro-ammeter readings and the number of ml of hydrochloric acid respectively, were plotted along ordinate and abscissa. An ordinary titration using an indicator (phenolphthalein) for establishing the end point, was carried out in parallel. Comparison of the results obtained by the two methods, showed that if one assumes the results obtained by ordinary titration to be correct, then the "error" of the H. F. titration is insignificant.

TABLE

Comparison of results of H. F. titration of NaOH solutions, and those of titration using phenolphthalein as indicator

Expt. No.	NaOH concentration	NaOH solution taken in ml	HCl used		% error
			for H. F. titration	with phenolphthalein as indicator	
1	0.1	10	11.25	11.2	+ 0.4
2	0.1	5	5.62	5.6	+ 0.3
3	0.1	10	10.63	10.6	+ 0.2

As can be seen from the results adduced, the "error" does not exceed ± 0.4%; this deviation is the result of more accurate readings of the volume of acid used for H. F. titration. If one disregards hundredths of a ml in the column "used for H. F. titration", then the results obtained by both methods coincide exactly.

Having established that the apparatus gives the most accurate and clear cut results on titrating with concentrations < 0.1 N (best of all with 0.01 N solutions), we tried an acid base titration in synthetic dark colored solutions, approximating in composition to those obtained under production conditions. The results obtained in these experiments did not differ in any respect from those obtained in the case of pure solutions of acids and alkalis; this enables one to forecast that H. F. titration will find application for analysis of acids and alkalis in many dark colored industrial solutions.

2. Determination of Saponification Coefficients

The H. F titration method proved to be a very good method for determining saponification coefficients of dark colored materials which are insoluble in water. Since the results we obtained may be of interest to organic analytical chemists, we have described below our experiments on the determination of saponification coefficients of synthetic resin samples. An aliquot of black resin, part of which was composed of rosin and castor oil, was dissolved in 25 ml benzene, and saponified for 3 hours with 25 ml of 0.5 N alkali. After saponification, the solution was made up to 100 ml with alcohol. (The solution was dark; ordinary titration gave variations of 10- 15% for duplicates. Electrometric titration proved to be out of the question, and gave low results because of precipitate formation, and rapid contamination of the electrodes).

5-10 ml of the alcohol-benzene solution obtained was pipetted out, made up to 50 ml with water, and titrated with 0.1 N HCl using the H. F. apparatus; the end point was determined by the intersection of the two straight lines on the titration curve.

Results for five determinations are given below.

Experiment No. 1. 0.6203 g of resin was dissolved in 25 ml benzene, and 25 ml 0.5 N alcoholic alkali added; the solution was heated under reflux for 3 hours and the resultant solution made up to 100 ml with alcohol. 5 ml of this solution was used for titration and required 4.25 ml of 0.1 N HCl. (In a blank test, 25 ml alkali required 22.63 ml of 0.5 N HCl). K was determined as follows.

$$\frac{4.25 \cdot 100 \cdot 1.0267^{*}}{5} = 87.27 \text{ ml } 0.1 \text{ N HCl or } 17.45 \text{ ml } 0.5 \text{ N HCl},$$

$$K = \frac{(22.63 - 17.45) \cdot 28}{0.6203} = 233.$$

Experiment No. 2. Sample weight was the same as in experiment No. 1; in this case, however, 10 ml of the final resin solution was taken for titration (see above); 8.5 ml of acid was used.

$$\frac{8.5 \cdot 100 \cdot 1.0267}{10} = 87.27 \text{ O.1 N HCl or } 17.45 \text{ ml } 0.5 \text{ N HCl},$$

$$K = \frac{(22.63 - 17.45) \cdot 28}{0.6203} = 233.$$

Experiment No. 3. Identical to the second. Saponification coefficient 233.

Experiment Nos. 4 and 5. 0.418 g of resin from another batch was treated in the same way as in the first experiment. 8.75 ml of acid was required to titrate 10 ml of final solution; the saponification coefficient was 239. A duplicate experiment gave identical results.

Ordinary volumetric titration gave a value of 178-261 for the saponification coefficient of the first batch, and 204-263 for the second. The theoretical saponification number for the first batch was 234, and 238 for the second; these practically coincide with the results obtained by means of H. F. titration.

3. Determination of Phenols and Cresols

We carried out over 30 experiments under varying conditions to determine the possibility of a rapid -

---

* 1.0267 — correction for the normality of the acid we used.

determination of phenols by means of H. F. titration. Though direct H. F. titrations of phenol with alkali gives results with an accuracy of ± 4%, all the same the end point is diffuse and there is considerable latitude in its determination on both sides. Accordingly we settled for a method involving preliminary treatment of test solution with alkali, followed by titration of test sample containing excess alkali and phenolate with acid. The experiments which follow below (3, 4, 5, 6, and 7) show that the method of H. F. titration of phenol can be carried out with an accuracy of ± 1.6%.

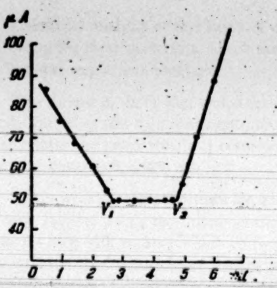


Fig. 1. Titration of phenol; V_1 = 2.8 ml — volume of HCl used for neutralizing the free alkali; V_2 = 4.8 ml — total 0.118 N HCl used.

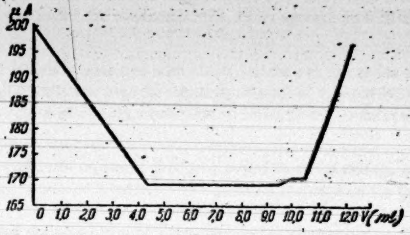


Fig. 2. Titration curve for technical cresol. The flat part at the second break — the final end point — corresponds to phenol present in the cresols as an impurity.

Experiments 3 and 4. 3.7019 g of pure phenol (calculated on a 100% phenol basis) was dissolved in distilled water in a standard flask, and the volume made up to 500 ml. 5 ml of this solution, containing 0.037019 g of phenol was used for titration, 10 ml of 0.113 N alkali solution was added, and the mixture shaken vigorously. 4.13 ml of 0.118 N HCl was used to titrate the phenolate; this corresponded to 0.0375 g phenol, or 101.3% of the theoretical value.

Experiment No. 5. 11.0212 g of technical phenol (on a 100% basis) was taken. After treatment with alkali, the solution was made up to 500 ml; 1 ml was taken for titration and made up to 50 ml. Two breaks were obtained on the titration curve (as in the previous experiment); the first point corresponded to acid used for titrating free alkali (2.8 ml); after the horizontal part there was a second clearly defined break (4.8 ml). 2 ml (4.8-2.8 ml) was therefore used in titrating the phenolate; this corresponded to 0.0222 g of phenol, instead of 0.0220, or 100.8% (Fig. 1).

Experiment No. 6 was identical to the fifth. The result was the same.

Experiment No. 7. 5.0 g of technical phenol, on a 100% basis, was treated with 13% sodium hydroxide and the volume of solution made up to 200 ml; 1 ml of solution contained 0.025 g phenol. 0.5 ml of 1.08 N HCl was used for titration; this corresponded to 0.0254 g phenol, or 101.6%.

In all tests with technical phenol, the phenol content was determined beforehand in test samples using a chemical method involving a bromide-bromate mixture; on the basis of chemical analysis, the test aliquot of phenol was calculated on a 100% phenol basis.

Experiment 1. 5.6949 g of a mixture of pure cresole consisting of 2.1021 g of meta-cresol, 2.4313 g of ortho-cresol, and 1.1600 g of para-cresol, was treated with 25 ml of 10% sodium hydroxide and the volume of solution made up to 50 ml. 1 ml of this solution contained 0.1139 g of cresols. 0.5 ml was taken for titration and the volume made up to 50 ml. 45 ml of 0.118 N HCl was used for titrating the cresols; this corresponded to 0.0574 g of cresol, i.e. 100.6% of theory.

Experiment 2. 0.25 ml of the solution prepared in experiment No. 1 was taken; 2.25 ml of acid was used for titration; this corresponded to 0.0281 g of cresol, i.e. to 100.6% of theory.

Experiment 3. 5.8842 g of technical tricresol was taken. This was treated with 30 ml of 10% NaOH; 1 ml of the cresolate solution contained 0.1525 g cresols.

6.25 ml of 0.118 N HCl was used to titrate 0.5 ml of this solution; this corresponded to 0.0797 g cresols, equivalent to 99.5% of the amount of cresol taken.

Experiment 4. 4.4153 g of test cresols was treated with 25 ml of 10% NaOH. 1 ml of this solution contained 0.1497 g cresols. 5.75 ml of 0.118 N HCl was used to titrate 0.5 ml of this solution; this corresponded to 0.07337 g of cresol, or 98.03%.

Chemical analysis of this batch of cresols showed that it contained 1.3% of neutral oil and 0.69% water; by allowing for these materials, which are not titratable under the conditions used, exact agreement with the experimental results was obtained.

Experiment 5. 0.77 g of technical dehydrated cresols was treated with alkali and the volume made up to 500 ml. 50 ml of this solution, containing 0.077 g of cresols was used for titration. 6.0 ml of 0.118 N HCl was used to titrate the cresolates; this corresponded to 0.0766 g of cresols, equivalent to 99.5% of the cresols taken. The cresol contained 0.45% oil.

While working out conditions for determining cresols in technical products, it was observed that on approaching the end point, the micro-ammeter readings increased regularly. This increase is shown on the graph by a small step with an area which corresponds to the phenol content of the cresole (Fig. 2). This happened in a number of exploratory experiments, and indicated the possibility of a simultaneous determination of phenol and cresols in their mixtures.

Work on improving the method for simultaneous determination of phenol and cresols continues.

SUMMARY

1. It has been shown that the H. F. titration assembly suggested by the Institute of Geochemistry of the USSR Academy of Sciences, is completely suitable for developing analytical methods for the control of plastics production.

2. A method has been worked out for determining acids and alkalis in dark colored solutions.

3. Express methods have been developed for determining phenol and cresols in technical products.

Received May 25, 1955

LITERATURE CITED

[1] V. A. Zarinsky and D. I. Koshkin, G. Anal. Chem., 10, 111 (1955) (T. p. 101)*.

POLAROGRAPHIC STUDY OF THE ELECTRODE REDUCTION OF NIOBIUM AND TITANIUM IN SULFURIC ACID SOLUTIONS

E. I. Krylov and V. S. Kolevatova

The S. M. Kirov Ural Polytechnical Institute

Modern methods for the colorimetric and gravimetric determination of niobium and titanium are complicated and difficult In this connection, some authors have studied the possibility of getting waves for titanium and niobium in various solutions, with the idea of using a polarographic method of analysis, as a comparatively rapid and fairly accurate method, which does not require complex chemical operations.

In 1953 Zeltzer [1], demonstrated the possibility of reducing titanium in acid solutions at a potential of −0.8V. According to Zeltzer, reduction follows the scheme

$$Ti^{4+} + e \rightarrow Ti^{3+}.$$

The second wave, which corresponds to further reduction of titanium to the potential at which hydrogen is liberated, was not detected by Zeltzer.

Nevertheless, individual authors have pointed out a number of difficulties which arise when polarographing is carried out in acid solution, as a result of the instability of titanium solutions caused by hydrolysis.

Thus, Strubl [2], during a study of the determination of titanium, discovered that the titanium wave-height increases somewhat with acidity in acid solution; this was explained on the basis of hydrolysis suppresion. In order to improve the shape of the titanium wave, and to avoid errors connected with hydrolysis, Strubl complexed titanium with tartaric and citric acids, respectively. When this was done, a straight line relationship was found to hold between wave-height and titanium concentration, over a fairly wide range. The half-wave potential of titanium, according to Strubl, lies at $E_1/_2 = -0.44$ V (relative to the saturated calomel electrode).

Zanko, Geller, and Nikitin [3], observed an instance of characteristic "aging" of acid solutions; e.g. in a solution in which the wave-height was originally 26 mm, after 24 hours, this dropped to 3 mm – acid solutions are unstable on account of hydrolysis. Apart from instability, sulfuric acid solutions were not suitable for polarography, the authors pointed out, because, in this case, the titanium waves were not clearly enough defined.

Accordingly, Zanko, Geller, and Nikitin [4], recommended that tartaric acid solutions be used for polarographic determination of titanium.

Cagliotti and Sartori [5], showed that it was possible to get a wave for titanium in alkaline solutions, by using sodium tartrate as complexing agent.

It has also been recommended in a number of other articles [6], that polarographic determination of titanium be carried out from complex solutions.

The polarography of niobium in acid solutions has been studied to a considerably lesser degree.

There are indications in the literature which suggest that it may be possible to get niobium waves, but only from nitric acid or complex solutions.

Thus, Zeltzer [7], found that niobic acid gives a clearly defined wave in 1 N HNO_3 at $E_{1/2} = -0.8$ V (relative to the saturated calomel electrode). The author suggests that reduction proceeds to Nb^{3+}. Zeltzer did not succeed in getting waves for niobium in either sulfuric or hydrochloric acid solutions respectively.

Portnov [8], pointed out that a niobium wave can be obtained in a nitric acid solution of niobate (in this case wave height is 36 times the normal value), but no wave is obtained in sulfuric or hydrochloric acid solutions. Portnov reckons that the wave is caused by separation of nitrate ions in the presence of niobium, and that only a semi-quantitative polarographic determination of niobium is possible.

Stromberg and Reinus [9], studied the possibility of a polarographic determination of niobium in various solutions: they established that no polarographic wave is obtained in solutions of hydrochloric, sulfuric, tartaric, and salicylic acids, nor in acid and ammoniacal solutions of oxalic acid and pyrogallol. The authors only managed to get a niobium wave in nitric acid solution. Nevertheless, the height of the niobium wave proved to be higher than that which could arise as a result of concentration polarization. This phenomenon was attributed by the authors to catalytic interaction of trivalent niobium with hydrogen ions. But, under known conditions, a proportionality could be observed between niobium concentration in solution and the height of its catalytic wave. This enabled the authors to conclude that polarographic determination of niobium in nitric acid solutions can give quantitative results.

Recently, Elson [10], published results on the reduction of niobium in tartrate and oxalate solutions, and also in KCl solution.

This short review of published results shows that cathodic reduction of niobium and titanium from their sulfuric acid solution has still only been studied to a limited extent, while the possibility of a quantitative determination of niobium and titanium by a direct polarographic method in sulfuric acid solution, has not been hitherto settled. In this connection, the necessity arose of carrying out a supplementary polarographic study of sulfuric acid solutions of niobium and tantalum, in addition to those carried out by us previously [11].

As cited above, individual authors have pointed out the difficulties which crop up during polarography of acid solutions of titanium, which are connected with the instability of its solutions as a result of hydrolysis. All this applies in equal degree to niobium. We managed to get over this question of hydrolysis by using concentrated sulfuric acid as solvent.

The investigations we carried out enabled us to detect clearly defined stable waves for niobium and titanium. It was assumed that the electrode reactions which occur, proceed according to the following schemes:

1. $Nb^{V} + 2e \longrightarrow Nb^{3+}$ and $Nb^{3+} + e \longrightarrow Nb^{2+}$.
2. $Ti^{4+} + e \longrightarrow Ti^{3+}$ and $Ti^{3+} + e \longrightarrow Ti^{2+}$.

There is no published information re the reversibility of these processes, since, hitherto, no success has been attained in getting a stable titanium wave (no niobium wave) in sulfuric acid solution. In addition, during a polarographic study of electrode processes of great importance is a knowledge of the mechanism of the electrochemical reduction of various ions – whether the electrode is reversible or irreversible. If the reaction is reversible, i.e. if no other form of polarization is observed apart from concentration polarization, then the electrode potential can be expressed by means of the thermodynamic equation for a polarographic wave

$$E = E_{1/2} - \frac{RT}{n \cdot F} \ln \frac{i}{i_d - i} \tag{1}$$

or at $t = 20°C$

$$E = E_{1/2} - \frac{0.05814}{n} \log \frac{i}{i_d - i}.$$

derived by Heyrovsky and Ilkovich [12].

It follows from this equation that on increasing the temperature, the half-wave potential ($E_{1/2}$) becomes more negative. This is one of the principal indications of the reversibility of an electrode process. An additional criterion of reversibility is the fact that the half-wave potential during ionic reduction should coincide with $E_{1/2}$ on the anode wave in the same medium.

On the other hand, if a graph is plotted of change in the value of E (at constant temperature) with logarithm $i/i_d - i$, then from the slope of the straight line obtained, it is possible to decide whether or not a process is reversible.

For reversible processes the slope should be equal to RT/nF, while, on the other hand, in the case of irreversibility – the slope will differ from the theoretical value.

The aim of the work described was to try and explain the mechanism of electrochemical reduction of the ions Nb(V) and Ti(IV) in sulfuric acid solutions on a dropping mercury electrode.

In our studies, we used both methods for clarifying the mechanism of these electrode processes.

EXPERIMENTAL

1. Preparation of Electrolyte Solutions

Sulfuric acid solutions of titanium and niobium were prepared as follows. Niobium pentoxide and titanium dioxide, taken separately, were fused with potassium pyrosulfate at 700°. After cooling, the melts were dissolved in 10% H_2SO_4. The solutions obtained were hydrolyzed by means of NH_4OH

Freshly precipitated titanic acid was dissolved on heating in 70% H_2SO_4, while niobic acid was dissolved in 96% H_2SO_4. After cooling, these solutions were made up to the required concentration by careful addition of water.

2. Apparatus and Method of Measurement

Polarograms were recorded on a micro-polarograph based on the Heyrovsky system; current-voltage curves were recorded automatically. Galvanometer sensitivity was 4.6 10^{-9} A/mm. The usual H-shaped vessel served as the electrolyzer. Mercury placed in the second arm of the vessel served as the second electrode (anode). Since the mercury surface was large enough (5 cm^2), anode potential remained constant during a measurement.

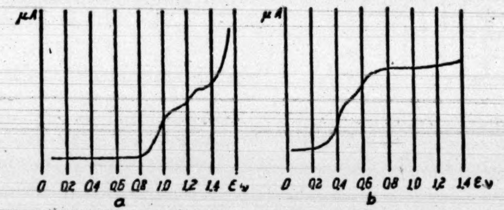


Fig. 1. Polarograms of sulfuric acid solutions of niobium (a) and titanium (b) $L = m^{2/3} \cdot T^{1/6} = 0.372\ mg^{2/3} sec^{-1}$.

Hydrogen was bubbled through test solutions for 15 minutes to remove oxygen before taking polarograms. A 0.5% acidified solution of gelatin, added in an amount sufficient to give a final concentration of ca. 0.0125% in the supporting electrolyte, was used as a maximum suppressor and for getting stable waves.

3. Experimental Results and Discussion of These Results

The first series of experiments on the study of the electrode reduction of Nb(v) and Ti(IV) in concentrated sulfuric acid was carried out at a constant temperature of 20°. Polarograms were taken of: a) niobium, containing 53mg/liter of Nb(V) in 70% H_2SO_4 (Fig. 1a); b) titanium containing 57.0 mg/liter of Ti(IV) in 66% H_2SO_4 (Fig. 1b); Solutions with these acid concentrations were stable; the phenomenon of "aging" noted by Zanko, Geller, and Nikitin [3], for titanium solutions, was not observed even in the course of a long period. Using the results of these experiments, we constructed graphs relating changes of potential E to logarithm $i/i_d - i$ (Figs. 2 and 3).

Analysis of the straight lines obtained showed that reduction of Nb^{5+} and Ti^{4+} ions in sulfuric acid solutions is irreversible, since the slope of the straight lines obtained differs from the theoretical values calculated by means of equation (1) (Table 1).

TABLE 1

Comparison of Theoretical and Experimental Values for the Slopes of the Lines Expressed by the Relation Between E and Logarithm i/i_{d-i} for niobium (V) and Ti (IV)*

Electrode reaction	Slope	
	Calculated on the basis of (1)	Found experimentally
$Nb^{5+} + 2e \rightarrow Nb^{3+}$	$\frac{0.05814}{2} = 0.02907$	0.072*
$Ti^{4+} + e \rightarrow Ti^{3+}$	$\frac{0.05814}{1} = 0.05814$	0.069**

* Mean of five determinations.

** Mean of four determinations.

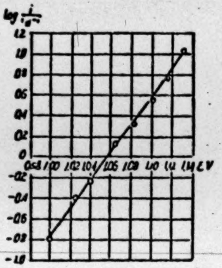


Fig. 2. Relation between potential E and logarithm i/i_{d-i} for the wave of niobium (V).

The aim of the second series of experiments was to determine the value of the shift in half-wave potential with temperature in the case of the electrode reactions studied. Measurements were carried out in a thermostat regulated to an accuracy of ± 0.1°. Results are given in Table 2.

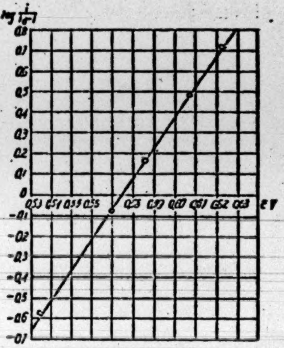


Fig. 3. Relation between potential E and the logarithm i/i_{d-i} for the titanium wave (IV).

TABLE 2

Relation between Half-wave Potential and Temperature

Electrode reaction	Half-wave potential* at °C			
	10	15	20	25
$Nb^{V} + 2e \rightarrow Nb^{3+}$	−1.0885	−1.0745	−1.0545	−1.0235
$Ti^{4+} + e \rightarrow Nb^{3+}$	−0.583	−0.578	−0.574	−0.572

---

* Potentials are referred to the saturated calomel electrode.

From these results it is clear that the half-wave potentials of both niobium and titanium are shifted to more positive values on raising the temperature. This fact also testifies to the irreversibilities of the reduction of Nb (V) and Ti (IV) respectively in sulfuric acid solutions.

SUMMARY

1. By a study of the relation between potential and logarithm $\frac{i}{i_{d-i}}$ it has been established that cathodic reduction of both niobium (V), and titanium (IV) in sulfuric acid solution, containing free sulfuric acid, is irreversible.

2. It has been shown that the magnitude and direction of the shift in the half-wave potentials $E_{1/2}$ of Nb(V) and Ti(IV) with increasing temperature, also testify to the irreversibility of the reduction of sulfuric acid solutions of these ions on a dropping mercury electrode.

Received June 18, 1954

LITERATURE CITED

[1] S. Zeltzer, Coll. Czech. Chem. Commun., 4, 319 (1932).

[2] R. Strubl, Coil. Czech. Chem. Commun., 10, 475 (1938).

[3] N. M. Zanko, B. A. Geller, and A. D. Nikitin, Factory Labs., 9, 976 (1940).

[4] N. M. Zanko, B. A. Geller, and A. D. Nikitin, Factory Labs., 13, 299 (1949).

[5] F. Cagliotti and G. Sartori, Cazz. Chim. Ital., 66, 741 (1936).

[6] Ya. P. Gokhshtein and A. M. Dymov, Trans. Comm. on Anal. Chem., 2 (V), 157 (1949); R. P. Gracham and A. Hitche, Analyst, 77, 533 (1952).

[7] S. Zeltzer, loc. cit.

[8] Portnov, Collection of Articles on the 20th anniversary of the State Institute of Applied Chemistry and State Institute of Chemical Technology, Leningrad 1939, p. 100.

[9] A. G. Stromberg and L. M. Reinus, J. Phys. Chem., 20, 693 (1946).

[10] R. Elson, J. Am. Chem. Soc., 75, 4193 (1953).

[11] E. I. Krylov, V. S. Kolevatova and V. A. Samarina, Proc. Acad. Sci. USSR, 98, 593 (1954).

[12] J. Heyrovsky and D. Jlkovic, Coll. Czech. Chem. Commun., 7, 198 (1935).

BLANK
PAGE

HIGH FREQUENCY TITRATION

A Q-METRIC ANALYTICAL METHOD

Yu. Yu. Samitov

The Ulanov Lenin Kazan State University

Many experimental and review articles, both Soviet [1-3], and foreign [4-10 et al], have been devoted to the application of high frequency electronics to volumetric analysis and physico-chemical studies. In the articles which have appeared during the period 1945-1955, most attention has been focused on the use of F-meters [11-15]; an appreciable number of papers have been devoted to the development of Z-meters, and apparatus of a mixed type [5, 11, 16-19]; Q-meters have been least developed.

Q-metric apparatus is the most simple with respect to technical construction, and the most convenient and least troublesome to operate. Thanks to its limiting simplicity, this method is available to a large circle of investigators who have not been specially trained in electronics. Altogether, only a few papers by foreign authors have been devoted to the application of Q-meters. Thus, Jensen and Parrack [20], have described an apparatus with a tuned grid circuit based on the anode current method. Anderson et al [21], used a generator with a tuned anode circuit based on the grid current method for acidimetric titration, and for titrations based on precipitation reactions. A similar scheme based only on anode current, was used by Blake [22], for studying diffusion rates in liquids. In physical studies apparatus of this type in the meter and decimeter range, are widely used for studying paramagnetic relaxation; in particular for the study of magnetic spin resonance [23]; attempts have also been made to use it for studying ionization potentials [24].

In Q-metric apparatus, use is made of the "soft" operating conditions of a tube generator, since under these conditions the direct components of the grid and anode currents of the generator, depend to a large extent on the goodness of the oscillating circuit. In most of the apparatus of this group, the titration vessel + solution is placed in a high frequency field of a capacity or induction coil, which are the direct elements of the oscillating circuit, and form together with the titration vessel, electrical C- or L- cells. With changing composition of test solution during reaction the value of the dissipated power of the electromagnetic field changes — this leads to a change in the quality of the circuit Q, and consequently to changes in the currents in the autogenerator circuit. In the general case the value of the power dissipated is determined, both by dipole losses, and by the specific conductivity of the test solution. Nevertheless, in most practical cases (for $\lambda > 1$ meter) dipole losses are insignificant [25], and the values of the grid and anode currents, and that of the voltage, are basically determined by the specific conductivity of the solution.

Description of a Q-Metric Set-Up

The Q-metric set-up used during the present investigation is shown schematically in Fig. 1; it consists of three basic loops: a H. F. generator of sinusoidal voltage, an electric cell of the C - or L- type, and a compensating circuit.

The 35 Mega-cycle Generator. Any scheme can, in practice, be used for the autogenerator. We used a triode generator operating on the three point Esau system. This set-up is characterized by its constructional simplicity and the ease with which oscillation in the meter and decimeter range can be obtained. When the generator is set up properly, it starts to work straight off as soon as it is switched on. Moreover, construction of the generator is not critical and no break-down of oscillation generation is observed. The induction coil L_k of the oscillating circuit was made from copper ribbon 0.96 mm thick and 3 mm wide; the number of turns was 6, while the diameter was 19 mm. In contrast to coils wound from round wire, coreless induction coils have high values of quality. The high effective quality of an oscillating circuit is known to be one of the basic requirements which determines the stability of generator frequency, and the excitation of harmonic oscillations in an auto-oscillating system. The coil was drawn outside the limits of the generator by means of a Lecher system. The semi-alternating capacitance in a circuit serves for coordinating the electrical cell with the anode circuit by choosing the generator

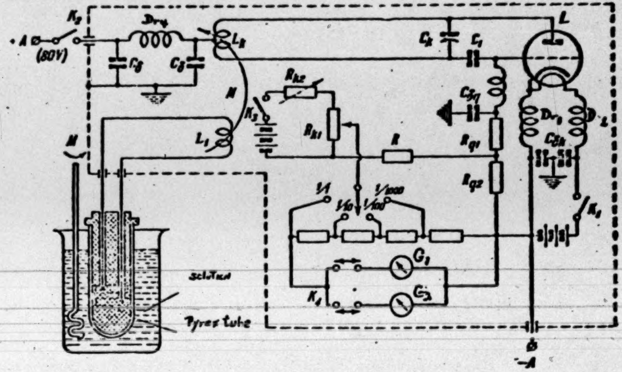


Fig. 1. Schematic diagram of the Q-metric oscillometer: $R_{g1} = 2{,}000\Omega$; $R_{g2} = 5{,}000\Omega$; $R_{k1} = 2{,}000\Omega$ (wire); $R_{k2} = 100\Omega$ (wire); $R = 5{,}000\text{-}10{,}000\Omega$; $C_k = 20\text{-}50$ pF; $C_1 = 100$ pF; $C_{\delta k} = 120$ pF; $C_{\delta g} = 120$ pF; $C = 50\text{-}70$ pF; D_{r1}, D_{r2}, D_{r3}, D_{r4} – high frequency chokes, 4 sections, 12 windings each, diameter of choke 7-9 mm; G_1) mirror galvanometer-type M-21/I ($C_i \approx 10^{-9}\text{-}10^{-10}$ A/mm/m); G_2) normal type galvanometer GMP ($C_i \approx 10^{-7}$ A/mm); L) 6H15 tube; M) mechanical glass stirrer.

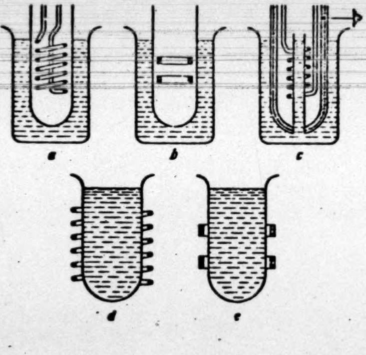


Fig. 2. Schematic construction of electrical C- and L-cells.

frequency. Coordination was carried out so that the measuring circuit (cell) is aperiodic with respect to the oscillation generator, while the operating point was located on one of the slopes of the resonance curve of the measuring circuit. Anode voltage was applied to the middle point of the induction coil circuit, through a H. F. sectionalized choking coil D_{r4}. The tube plate was supplied from a high capacity acid accumulator (EST-112). A rectifier with an electronically stabilized voltage supplied the anode [26]. In addition, a 75 C5-30 stabilivolt was connected to the output of the stabilizer. Anode and plate voltage were always lower than the normal values for the given tube; accordingly, there was no essential heating of the tube, which usually leads to instability in generator operation. These last precautions ensured stable operation of the generator, and high sensitivity to wattage losses.

A cathode tube with low grid currents (one half of a double triode 6H-15) was used as the autogenerator. To avoid difficulties connected with poor contact between tube tappings and connections on the tube panel, the latter were not used; the apparatus was set up carefully by soldering the elements of the apparatus directly to the tube tappings. All the apparatus and supply source were carefully screened. The generator was switched on 20-30 minutes beforehand, to warm up.

The Electrical Cell. Hitherto only the simplest electrical cells with variable charging coefficients (Figs. 2d and e) have been described in the literature; the construction of these cells complicates thermostating of the test system*. We should therefore like to suggest three new types of electrical C- and L-cells, which have a constant charging coefficient (Figs. 2a, b, and c) which can be called immersion cells. In these cells, the arrangement of the electrodes with respect to the insulating pyrex tube is always the same; accordingly, when such cells are immersed in a test solution, the liquid is always arranged in the same way with respect to the cell electrodes, as long as its level is 1-1.5 cm higher than the upper edges of the electrodes. The cells suggested, in contrast to the other two types of cells used formerly, permit easy thermostating of test system, and permits one to switch from relative measurements to electrical conductivity to absolute measurements. Electrical L-cells of type a and c, differ from each other in that, in the first case the solution is under the influence of an "exterior" alternating magnetic field, while in the second case, the solution is influenced by an "internal" alternating magnetic field. As it turned out, this difference is significant. What it boils down to is that in the alternating magnetic field of any real solenoid, there exists an uncompensated electrical field, directed along the axial axis of the coil. Symmetry conditions for the inner part of the induction coil is better than for the peripheral region. As a consequence of this, in cells of type a, the liquid finds itself in the sphere of action of both a magnetic field, and of an appreciable electrical field; in the case of type c cells the liquid is protected from the effects of the peripheral field by an earthed screen, and is only affected by the internal magnetic field, in which there is only an insignificant uncompensated electric field. Thanks to the last characteristic feature, the capacity effect, which is manifested on immersion of a cell in a liquid with a high dielectric constant, (e.g. water, $\epsilon^{20°C} = 80$) is considerably smaller in the second case than in the first. By suitable coordination of the cell with the anode circuit, it is possible, as was found experimentally, to be rid of the capacity effect altogether. To decrease the capacity effect of the operator himself, and the operating circuit, it is recommended that cells a, b, d, and e + titration vessel should be protected by an electrostatic screen.

---

* The electrical C-type cell of Blake [6], which was also recently used by Zarinsky and Koshka [3], is, to some extent, free from these drawbacks; nevertheless, it still has the drawback, that some of the solution remains on the inner wall of the conductometric tube.

Cells b and e are usually used for titration, while cell c is used for studying the kinetics of certain oxidation-reduction reactions. An inductance coupling is used between the electrical cells and the anode circuit of the generator.

Compensating Circuit. Measurements of wattage loss in the oscillating circuit were carried out by means of grid or anode current, using the ordinary type of compensating circuit [3, 23]. For convenience of operation, the current to be measured is led to the galvanometer through a universal shunt, which permits the sensitivity of the galvanometer to be lowered, without producing hardly any change in its external critical resistance, to three successive places. The null galvanometer G_2 was used, as a rule, only for compensating initial grid current.

Some Results from the Theory of a Q-Metric Generator

To clarify the factors which determine the sensitivity of a generator to wattage losses, and the possibilities of using a Q-metric apparatus for conductometric measurements, we made a theoretical analysis of the measuring generator [27, 33].

For analysis, we used the linearized characteristics of the tube generator, and assumed that the power absorbed by the test solution amounted to not more than 0.5-1%. The latter condition is obtained by placing the cell containing a small amount of dilute solution in the induction coil circuit, or by immersing the electrical C- and L-cells, inductively connected with the circuit, in the test solution. In these cases, according to published results [29], it is possible to disregard changes in the intensity of generator oscillations, and to reckon that the mean oscillating power, given out in the induction coil, changes at the expense of the effective active resistance introduced into the circuit by the sample. We verified the correctness of this last assumption in the course of special tests.

When an electrical L-cell is used, the following linear relations hold between changes in the direct component of the grid

$$\Delta I_{do} = -K\Delta\kappa,$$
$$\Delta I_{do} = m\Delta\kappa, \qquad (1)$$

for $R_2 >> \omega L_2$,

where $K = \frac{b}{\pi}(\sin \psi_g - \psi_g \cos \psi_g) V_{a1} \frac{R_i}{\alpha_1 \cdot \mu} (\omega q)^2 C_k L_2$, $m = \frac{V_{a_1}}{\alpha_1} \cos \psi_g (\omega q)^2 C_k L_2$ — are constant coefficients. Here, b — is some constant, whose value is determined by the detecting properties of the cathode-grid interspace of the generator tube; ψ_g — the cut-off angle of the grid current; V_{a1} — the amplitude of the first harmonic of the anode voltage; α_1 — the coefficient of the first harmonic; R and μ — respectively, the internal resistance of the amplification factor of the generator tube; q — the charging coefficient of the cell; ω — the cyclical oscillation frequency; L_2 — an arbitiary inductance, whose values if solely determined by the geometric dimensions of the cell, and the amount of electrolyte poured into it; R_1 — some arbitrary resistance, whose value is determined by the specific resistance of the solution (for a more detailed consideration of the values of L_2 and R_2, see [2], remembering that L_2 and R_2 in formula (1) correspond respectively to L_1 and R_1 in [2]).

Thus, the limits of linearity of the set-up are determined by the conditions $R_2 >> \omega L_2$, which corresponds to the region of fairly dilute solutions. In order to interpret titration results in more concentrated solutions, it is necessary to take into account the shape of the characteristic curve.

The Characteristic Curve

When the concentration of a solution changes within small limits, there occurs a corresponding linear change in grid or anode current. Nevertheless, when the concentration of the solution is varied within wide limits, the readings of the apparatus in the grid and anode circuits of the generator, pass through a maximum when C-cells are used, and through a maximum and a minimum when L-cells are used. Accordingly, when an arbitrary choice is made of the initial concentrations of the components of the reaction mixture, and the operating point is near the maximum of the characteristic curve, the titration curves may be distorted. In order to generalize results re the relation between the position of the maximum relative to the concentration axis, with type of electrolyte and temperature conditions respectively, and to explain its physical nature, various series of measurements were made for the following arrangements of the electrical cell with respect to the circuit: a) the cell + solution or reaction mixture was placed directly in the anode circuit, or in the electrical field of a condenser, connected to the terminals of the induction coil of the generator oscillating circuit; b) the cell was placed in the induction coil, or in the capacity field, connected inductively to the oscillating circuit; c) and, finally, the insulated coil or capacitance, connected inductively with the oscillating circuit, was immersed in a pyrex beaker containing test solution, which in turn was immersed in a thermostat whose temperature was maintained constant by means of mercury-toluene thermoregulator and an electronic relay, with an accuracy of ± 0.05°.

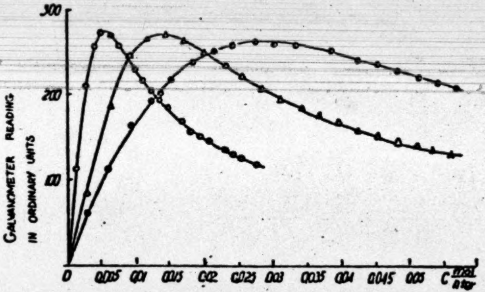


Fig. 3. Characteristic curves: O) HCl; Δ) NaOH; ⊘) NaCl; C) cell type B; $f = 35.0 \cdot 10^6$ Hz; $t = 20 \pm 0.05$°C.

In all cases where C-cells were used, characteristic curves with a maximum were obtained. Some of these are shown in Figs. 3 and 4. Table 1 contains the collected results obtained by Reilley [5], by the impedance bridge, and by the author by means of a Q-metric oscillometer. The relaxation times of the ionic atmosphere given in Table 1 under the designation τ_{expt} were calculated by means of Falkenhagen's formula [28]

$$\tau = \frac{8.85 \cdot 10^{-11} D}{C \Lambda_0}, \tag{2}$$

where D — is the dielectric constant of the solvent; C — normal concentration; Λ_0 — the limiting equivalent electroconductivity. Molar concentration C• is substituted in formula (2) for calculating the relaxation time τ_{expt}; this molar concentration corresponds to the position of the maximum on the characteristic curves, whose values are also given in the same table.

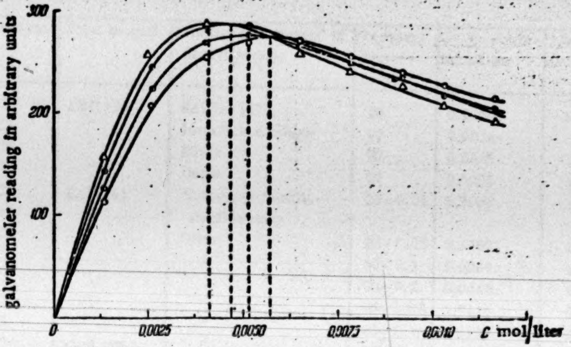


Fig. 4. Displacement of the position of the maximum on the characteristic curves with temperature. Hydrochloric acid: ○) 20 ± 0.05°C, ◐) 25 ± 0.05°C, ⊙) 30 ± 0.1°C, Δ) 35 ± 0.2°C; f = 35.0 Mega-cycles C) cell type B.

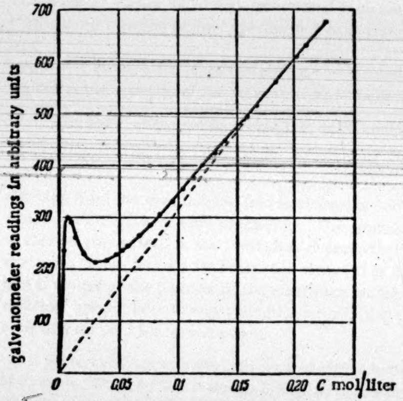


Fig. 5. Characteristic curve. Hydrochloric acid: L-cell type (D); f = 35.75 mega-cycles.

The following regularities were discovered by an analysis of the results obtained:

a) characteristic curves of various electrolytes referred to the system of coordinates $G_p \times \kappa$ (H. F. conductivity x specific conductivity for $\underline{t}$ = constant, do not fuse into each other; this does not agree with the theory of equivalent schemes for C-cells; b) the specific conductivities $\kappa^{\bullet}$ correspond to the maximum of the characteristic curves at various temperatures; but for f = constant (35 Mega-cycles) have, within the limits of experimental accuracy, for a given type of electrolyte, one and the same value (for the temperature range 15-35°); c) the relationship between the values of the concentration at the maximum $C^{\bullet}$ and the temperature $\underline{t}$, for the electrolytes tested, is linear: $C^{\bullet} = \alpha - \beta t$, where α and β – are certain constants (field frequency is a parameter of this family of straight lines); d) between the values of H. F. conductivity $G_p^{\bullet}$ and the specific conductivity $\kappa^{\bullet}$ at the maximum, and the frequency of the H. F. field there exist the following proportionalities $G_p^{\bullet} = a\omega$ and $\kappa^{\bullet} = b\omega$ (in the frequency range f = 1–35 Megacycles).

These results show that the equivalent scheme for an electrical C-cell given by Reilley [2,5], does not describe the regularity (point a) observed experimentally, fully enough. This conclusion is obvious, since not one distributed system, of which a titration vessel + solution is an example, can be represented by a simple equivalent circuit with concentrated values.

As a result of a detailed analysis of the regularities obtained, the following semi-empirical relation [27], was obtained, which describes the position of the maximum on characteristic curves:

$$\kappa C^{\bullet} = 23.29\,\frac{D}{\Lambda_0} \qquad (3)$$

TABLE 1•

Experiment number	Electrolyte	Type of cell	Author and method of investigation	Temperature•• in °C	C• g• equivalents-liter	$1/\omega \cdot 10^8$ seconds	$\tau_{\text{exptl.}} \cdot 10^8$ sec	$\kappa^{\bullet} \cdot \mu\Omega^{-1} \cdot \text{cm}^{-1}$
1	KCl	Cell (E)	Reilley [5]	20	0.0004	15.9	12.2	60
2	KCl	"	Impedance bridge	20	0.0014	5.5	3.9	160
3	KCl	"	Ditto	20	0.0046	1.6	1.16	580
4	KCl	"	Ditto	20	0.0095	0.8	0,55	1125
5	HCl	Cell (B)	Author: Q-metric oscillometer	20 ± 0.05	0.0058	0.45	0.31	2160
6	HCl	"	Ditto	25 ± 0.05	0.0052	0.45	0.31	2150
7	HCl	"	"	30 ± 0.1	0.0047	0.45	0.31	2145
8	HCl	"	"	35 ± 0.2	0.0042	0.45	0.32	2155
9	KCl	"	"	25 ± 0.05	0.0145	0.45	0.32	1925
10	KCl	"	"	30 ± 0.1	0.0128	0.45	0.32	1930
11	KCl	Cell (E)	"	22	0.0150	0.45	0.33	1750
12	NaOH	Cell (B)	"	20 ± 0.05	0.0137	0.45	0.27	2700
13	NaCl	"	"	20 ± 0.05	0.0214	0.45	0.30	2100

• The values of the dielectric constant of water D for various temperatures, which were required for calculating $\tau_{\text{exptl.}}$ were taken from a handbook [30]. The equivalent conductivities Λ_c were taken from the monograph [31]. The value of Λ_0 for NaOH was determined from ionic mobilities.

•• Since no mention of the experimental temperature is made in [5], we assumed that it was 20° (room temperature).

here λ – is the wave length in cm ; C• – the molar concentration of the electrolyte at the maximum point; D – the dielectric constant of the solvent; Λ_0 – the limiting equivalent conductivity of a one-one valent electrolyte.

The semi-empirical formula (3) is more complete than the empirical formula

$$\lambda C^{\bullet} = K, \tag{4}$$

obtained from the calorimetric measurements of Forman and Crisp [32], where K – is some constant which is determined individually for each electrolyte. Our formula takes into account both the temperature conditions and type of electrolyte, as well as the individual characteristics of univalent electrolytes. In essence, formula (3) is analogous to the formula for relaxation time (2) in the dispersion theory of Falkenhagen, but, with the difference that it describes the position of the maximum on the characteristic curves accurately. Formula (3) is useful both for titration and for kinetic experiments for evaluating the straight line part of the characteristic curve of the generator-oscillometer used for measurement.

More complex relationships were observed between electrical L-cells and apparatus readings, than in the case of C-cells. One of these is shown in Fig. 5. Characteristic curves, drawn on the basis of grid and anode currents, resemble each other in shape (if the correct scale is chosen, they appear to be mirror images of each other). Relaxation times, calculated on the basis of the experimental values for the concentration C• of various electrolytes, have, for ω = constant, different values. On the basis of this fact, we concluded that in this case, the curves are obtained as a result of the superposition on the basic measurement of the effect, of an uncompensated electrical field which is always present in the field of a real solenoid.

Application of the Method

Q-meters can be used in volumetric analysis, in those cases where there exists a difference between the value of the electro-conductivity of the reaction mixture at the beginning or the end of a titration, and that at the equivalence point. In such cases, small changes in conductivity of the solutions which occur during neutralization, precipitation, and oxidation-reduction reactions, are fixed with a high degree of accuracy. The use of electrical cells, in which there is no direct (galvanic) contact between cell electrodes and solution, completely eliminates complications and errors, such as electrolysis of the solution with accompanying instability of the apparatus, and contamination of the electrodes with precipitate particles, which occur in other physico-chemical methods involving the use of electrodes which are immersed in the solution.

The author, in conjunction with V. M. Gorokhovsky, carried out an all-round study of the possibilities of the method developed in volumetric analysis and in chemical kinetics. As we showed experimentally, if the range of measurements does not overstep the straight line part of the characteristics curve up to the maximum, then H. F. conductometric analysis will have obvious advantages over other methods, allowing very dilute solutions and natural products to be analyzed.

Thus, the limiting absolute error ϵ, and the relative error δ obtained on carrying out a mathematical analysis of a large number of results obtained during argentometric titration, had the following values:

a) Solutions of potassium ferricyanide: $C_x \sim 10^{-3}$ M; $\epsilon = \pm 0.00004$ M;
$\delta = \pm 1.3\%$; $C_x \sim 10^{-4}$ M; $\epsilon = \pm 0.000005$ M; $\delta = \pm 1.6\%$;

b) Solutions of ammonium cyanate: C_x 10^{-3} M; $\epsilon = \pm 0.0001$ M; $\delta = \pm 4.6\%$;
$\delta = \pm 1\%$; $C_x \sim 10^{-4}$ M; $\epsilon = \pm 0.00005$ M;

c) Solutions of potassium iodide: $C_x \sim 10^{-2}$ M; $\epsilon = + 0.0008$ M;
$\delta = \pm 0.7\%$; $C_x \sim 10^{-3}$ M. $\delta = \pm 1\%$; $C_x \sim 10^{-4}$ M; $\delta = \pm 3\%$.

The method developed was also used for studying the kinetics of some oxidation reactions of organic acids by potassium permanganate. It is well known that these reactions are exceptionally sensitive to contamination inevitably brought in on pipet tips during titration of test samples, and to the presence of metal electrodes, which speed up the reactions, thereby distorting its normal course, first near the electrodes, and then throughout the whole bulk of the solution. The use of non-conducting electrical cells, in whose weak electric field, which does not have a measurable effect on the velocity of chemical transformation, the test system is found, has shown that the H. F. method holds great possibilities for the study of chemical kinetics also.

SUMMARY

1. A Q-metric variant has been developed for H. F. analysis.

The theory of Q-metric analysis is given. The construction of three new types of electrical cells with constant charging coefficients has been described, whereby it is easy to thermostat the system studied, and which makes it possible to carry out various conductometric measurements at high frequencies.

2. The relationships between H. F. conductivity and the concentration and temperature have been experimentally established, using some one-one valent electrolytes. On the basis of an analysis of the experimental material obtained, and of other material published in the literature, a semi-empirical formula $\lambda C^{*} = 23.29\, D/\Lambda_0$, has been derived which describes the position of the maximum on the characteristic curve. This formula allows one, before carrying out a titration, to determine the working part of the characteristic curve, and to forecast the shape of the titration curve for different temperatures and frequencies.

Received November 22, 1954

LITERATURE CITED

[1] G. V. Troitsky, Biochemistry, 5, 373 (1940).

[2] O. L. Kaptsan and V. A. Teplyakov, J. Anal. Chem., 8, 131, (1953) (T. p. 151)*.

[3] V. A. Zarinsky and D. N. Koshkin, J. Anal. Chem., 9, 29 (1954) (T. p. 29)*, 10, 111 (1955).

[4] J. Weber, K. Keith and J. Laidler, J. Chem. Phys., 19, 1087 (1951) (T. p. 101)*.

[5] C. N. Reilley and W. H. McCurdy, Jr., Anal. Chem., 25, 86 (1953).

[6] J. L. Hall, Anal. Chem., 24, 1236 (1952).

[7] R. C. Axtmann, J. Am. Chem. Soc., 73, 5367 (1951).

[8] Soichiro Musha, Science Rep. Research Insts. Tokyo Univ., Ser. A, 4, 575 (1952).

[9] K. Cruse, Z. anal. Chem., 133, 361 (1951).

---

* T. p. = C. B. Translation pagination.

[10] K. Cruse. Z. anal. Chem., 136, 129 (1952).

[11] J. L. Hall, Anal. Chem., 24, 1244 (1952).

[12] P. W. West, P. Senice and T. S. Burkhalter, Anal. Chem., 24, 1250 (1952).

[13] W. F. Wagner, and W. B. Kauffman, Anal. Chem., 25, 538 (1953).

[14] W. J. Blaedel and H. V. Malmstadt, Anal. Chem., 22, 734 (1950).

[15] W. J. Blaedel and H. V. Malmstadt, Anal. Chem., 22, 1413 (1950).

[16] G. G. Blake, The Analyst, 75, 32 (1950).

[17] J. L. Hall and J. A. Gibson, Anal. Chem., 23, 966 (1951).

[18] O. I. Milner, Anal. Chem., 24, 1247 (1952).

[19] G. G. Blake, Analyst, 75, 633 (1950).

[20] F. W. Jensen and A. L. Parrack, Ind. Eng. Chem., Anal. Ed., 18, 595 (1946).

[21] K. Anderson, E. S. Bettis and D. Revinson, Anal. Chem., 22, 743 (1950).

[22] G. G. Blake, J. Sci. Inst., 24, 77 (1947).

[23] S. G. Salikhov, J. Expt. Theor. Phys., 17, 1070 (1947).

[24] E. K. Zavoisky, J. Expt. Theor. Phys., 6, 477 (1936).

[25] M. A. Divilkovsky and D. I. Mash, J. Expt. Theor. Phys., 10, 520 (1940).

[26] A. N. Bonch-Bruevich, "The Application of Electron Tubes in Experimental Physics", Moscow-Leningrad, 1950, p. 474.

[27] Yu. Yu. Samitov, Author's Thesis, Kazan, 1954.

[28] Falkenhagen, "Electrolytes", Gen. Sci. Tech. Press, 1935, p. 275; V. V. Semenchenko, "The Physical Theory of Solutions", State Theor.-Tech. Lit. Press, Moscow-Leningrad 1941, p. 183.

[29] Radiotechnics Notebook edited by V. A. Smirenin, Moscow-Leningrad 1950.

[30] V. I. Perelman, "Brief Chemist's Notebook", State Chem. Press, Moscow-Leningrad 1951, p. 342.

[31] G. Harned and B. Owen, "The Physical Chemistry of Electrolyte Solutions, State Press for Foreign Tech. Publications Moscow, 1952, p. 558.

[32] J. Forman, and D. J. Crisp, Trans. Faraday Soc., 17A, 186 (1946).

[33] A. G. Shafigullin, "The Application of Physical Methods in Chemical Kinetics", 1955, p. 136.

A CHROMATHERMOGRAPHIC METHOD OF SEPARATING HYDROGEN, CARBON MONOXIDE, METHANE, AND MIXTURES OF INERT GASES

N. M. Turkeltaub, O. V. Zolotareva, A. G. Latukhova, A. I. Karytova, and E. R. Kalnina

The All-Union Scientific Research Institute of Petroleum Geology and Prospecting, Moscow

Individual determination of hydrogen, carbon monoxide, methane, and inert gases is important in the various branches of industry — petroleum, chemical, and electro-vacuum.

On using a chromathermographic method of analysis [1], hydrogen and carbon monoxide separate together with methane. Accordingly, it is necessary to carry out an additional analysis of the fraction containing hydrogen and carbon monoxide by means of the All-Union Heat Engineering Institute apparatus.

Existing methods of determining rare gases reduce to a separation of helium and part of the neon by adsorbing the remaining components on charcoal at the temperature of liquid nitrogen.

Chromathermographic separation of the gases mentioned above has been discussed recently in the work of J. Janak [2]; he demonstrated the possibility of carrying out a chromatographic analysis of a mixture of rare gases, carbon monoxide, and hydrogen. Nevertheless, the method Janak used, in which CO_2 was used as the developer, and the separated gases were measured in a buret, does not permit separation of carbon monoxide and argon, from hydrogen and nitrogen.

The method described in the present article differs from Janak's method in the use of other developers and fixing apparatus, as well as carbon dioxide, and the application of chromathermography, which leads to an essential improvement in separation, and permits analysis to be carried out without resort to the use of low temperatures. For this purpose, it is essential to use an adsorbent with a high capacity for poorly sorbed materials. Activated charcoal of the following makes were tested as potential adsorbents: fine pore and coarse pore mark AG, and mark KAD charcoal. The charcoal was given a preliminary drying at 200° to constant weight. After this treatment it is activated for 8 hours by evacuation with a vacuum pump (the vacuum was of the order of 10^{-3} mm Hg) and heating to 400°.

The method of test used was as follows: in a vertical glass column was placed a known amount of activated charcoal. Onto this adsorbent, at room temperature, was placed a definite amount of hydrogen, carbon monoxide, methane, or one of the rare gases, or a mixture of these gases, after which the chromatogram was developed either with air or carbon dioxide, with simultaneous forward movement of an electric oven, inside which a temperature gradient was maintained. For development with carbon dioxide, chromathermograph model No. 4 [3] was used. The apparatus used for fixing in this instance was a micro-buret filled with 40% KOH. Carbon dioxide was absorbed by the alkali, while the amount of desorbed gases was measured in the micro-buret.

When the chromathermograms were developed with air, the apparatus used for fixing was that based on measurement of thermal conductivity of the gases; in addition, a thermochemical gas analyzer was used for fixing; this was based on the thermal effects of combustion.

The apparatus used for the investigation is shown schematically in Fig. 1.

A: Separation of Hydrogen, Carbon Monoxide, and Methane

A definite amount of hydrogen, carbon monoxide, and methane (from 0.5 to 5 cm^3) was placed on 57 g of coarse pore AG charcoal, after which the chromatogram was developed with air at a rate of 100 cm^3/minute. A continuous thermochemical gas analyzer was used for fixing.

To determine completness of desorption, the same amount of test material which had been placed on the charcoal in the test run, was drawn through the empty tube; air was then drawn through this tube. The fixing

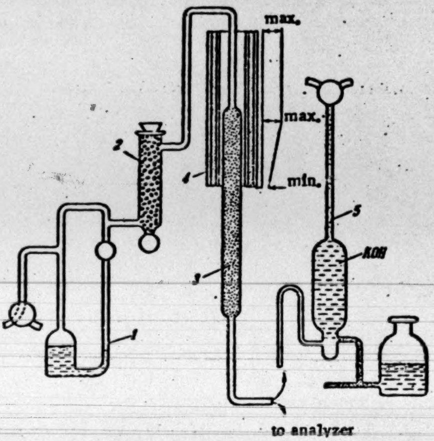


Fig. 1. Chromathermograph No. 4: 1) rheometer; 2) drier with $CaCl_2$; 3) column + adsorbent; 4) electric oven; 5) micro-buret + 40% KOH.

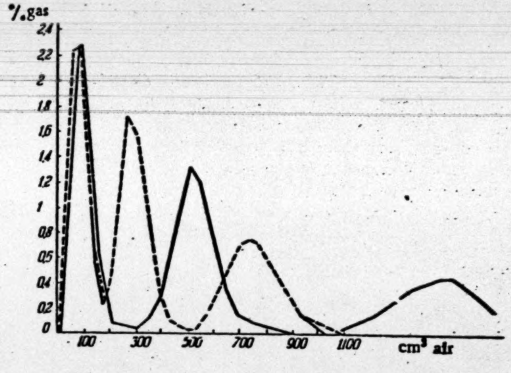


Fig. 2. Output curve for a mixture of hydrogen — carbon monoxide — methane — air.

apparatus was fitted at the outlet so as to take the curve of the issuing gases. The coincidence obtained between the area of the output curve for passage of the gas through tube containing adsorbent, and through the empty tube, respectively, testified to the completness of desorption. Hydrogen is not adsorbed at all by charcoal at ordinary temperatures. For a developer rate of 100 cm³/minute through 57 g of coarse pore AG charcoal, hydrogen at a concentration of 1% comes off while the gas mixture is being applied to the adsorbent. Maximum hydrogen concentration on the output curve for the tube was observed after passage of 150-300 ml of air through the column. Under the same condition, carbon monoxide started to come off after 250 cm³ of air had been passed through; its maximum concentration on the output curve was attained after the passage of 350 cm³ of air; 550-600 cm³ of the eluting air was required for complete desorption.

TABLE 1

Charcoal AG, 48 g: $v_{air} = 100$ cm^3/minute

Experiment number	Composition of gas mixture	Volume of developer used before gas starts to come off	Volume of developer used to complete elution of gas	Amount taken in cm^3	Amount found in cm^3	Observations
1	Hydrogen	0	215	1.00	0.90	Dry
	Carbon monoxide	215	600	1.00	0.90	
2	Hydrogen	0	250	3.00	3.00	Dry
	Carbon monoxide	250	600	0.50	0.50	
3	Hydrogen	0	250	0.50	0.45	Dry
	Carbon monoxide	300	800	4.00	4.00	
4	Carbon monoxide	315	800	5.00	5.10	Dry
	Methane	1100	2000	0.50	0.45	
5	Hydrogen	0	200	2.10	2.20	Dry
	Carbon monoxide	300	800	2.10	2.20	
	Methane	1100	2000	2.0	1.90	
6	Carbon monoxide	200	600	5.00	5.00	Moist
	Methane	600	1000	0.50	0.50	
7	Hydrogen	0	200	2.10	2.20	
	Carbon monoxide	200	500	2.10	2.20	Moist
	Methane	500	1100	2.00	1.90	Moist

TABLE 2

KAD Charcoal, 94 g: $v_{CO_2} = 40$ cm^3/minute

Experiment number	Composition of the gas mixture	Volume of developer used before gas starts to come off in cm^3	Volume of developer used to complete elution of gas in cm^3	Amount taken in cm^3	Amount found in cm^3
1	Hydrogen	40	340	10.2	10.3
	Air	360	500		
2	Hydrogen	140	340		
	Air	360	480	6.3	6.2
3	Air	240	380	21.0	21.1
	Methane	600	1120		
4	Air	240	400		
	Methane	600	1120	21.1	21.3
5	Hydrogen	80	260		
	Air	280	420	9.7	9.7
	Methane	660	940		
6	Hydrogen	60	260		
	Air	260	400	21.3	21.3
	Methane	600	1060		
7	Hydrogen	60	260	21.3	21.3
	Air	280	420		
	Methane	600	1020		

Methane started to come off after 600 cm^3 of air had been passed through; its maximum concentration on the output curve was observed after passage of 950 cm^3 of air, while complete desorption was only achieved after 1200 cm^3 of air had been passed.

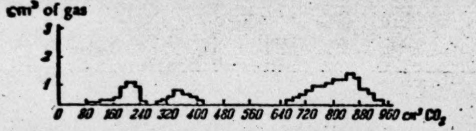


Fig. 3. Output curve for a mixture of hydrogen — air — methane.

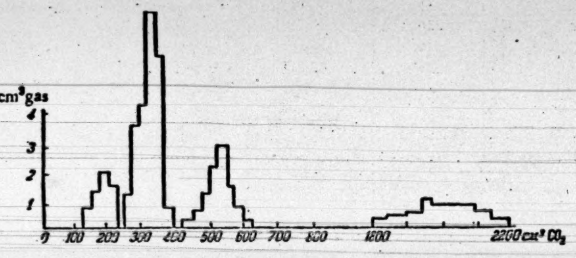


Fig. 4. Output curve for a mixture of helium — argon — krypton — xenon.

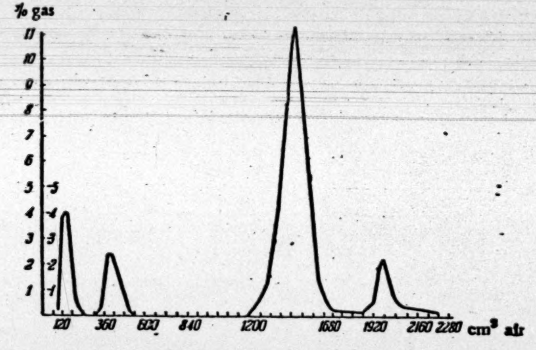


Fig. 5. Output curve for the mixture argon-helium — krypton and xenon.

Thus, 57 g of coarse pore AG charcoal proved insufficient to guarantee complete separation of hydrogen, carbon monoxide and methane. 48 g of fine pore AG charcoal was next tried. Here again, hydrogen was not adsorbed at all. In this case however carbon monoxide and methane were appreciably better adsorbed than on the coarse pore charcoal. Carbon monoxide started to come off after passage of 500 cm³ of air, while methane only came off after 1200 cm³ of air had been used.

The effect of the ratios between H_2, CO, and CH_4 on completness of separation was studied. Table 1 shows that on changing the ratio of the individual components a few times, separation of components becomes possible.

We thought it would be of interest to find out the nature of the sorption and the reason for the separation of hydrogen, carbon monoxide, and methane, at room temperature, in particular the reason for the high degree of sorption of carbon monoxide in comparison with nitrogen. The assumption was made that as a consequence of the presence of oxides of a basic character on the surface of the charcoal, sorption of carbon monoxide is of the activated adsorption type.

To check this assumption, charcoal was specially left in damp air for 19 hours; this should lead to an increase in the number of oxide groups on the charcoal surface. Nevertheless, blocking of adsorption places by water proved to be stronger, as can be seen from Fig. 2, in which the continuous line represents separation on dry charcoal, while the dotted line represents what happens when the charcoal underwent the treatment just described.

It could be postulated that at room temperature physical adsorption of carbon monoxide on the charcoal occurs.

Separation of hydrogen, carbon monoxide, and methane was also tested on 94 g of dry charcoal type KAD. Better separation was attained and complete desorption was achieved. In order to speed up analysis, development was carried out by eluting with air and simultaneously moving forward an electric oven, at a maximum temperature of 100°, along the adsorbent layer at the rate of 3 cm/minute.

Determination of the amount of material by integrating the areas at low concentrations is fairly tedious. Moreover, a continuous gas analyzer is not always available. Accordingly we adopted the method of measuring individual portions directly in a buret filled with alkali [4-6].

Table 2 and Fig. 3 illustrate the results obtained, during separation of the gases indicated on 94 g of KAD charcoal when the developer velocity was 40 cm^3/minute.

Carbon monoxide was not separated from nitrogen and hydrogen under these conditions.

Time taken for a complete analysis was 30 minutes. Analytical accuracy was limited by accuracy of measurement, completness of absorption, and the purity of the carbon dioxide. Relative analytical error was 0.3%.

B. Separation of the Rare Gases

On the basis of a chromathermographic method of separating and analysing a mixture of hydrocarbon gases developed previously, a technique was worked out for the separation of mixtures of rare gases into their components. For this purpose 94 g of KAD charcoal was used as the adsorbent. Either carbon dioxide or air was used as developer. Output curves were taken for helium, neon, argon, krypton, and xenon and their mixtures.

Fig. 4 represents an output curve obtained for the rare gases. For a rate of developer CO_2 (v) = 50 cm^3/minute, and a rate for the forward movement of the electric oven of (w) = 3.0 cm/minute, and a maximum oven temperature (t_{max}) = 290°, helium started to come off after 125 cm^3 of carbon dioxide had been passed through; 250 cm^3 of carbon dioxide was sufficient to remove helium completely from the adsorbent. Neon came off practically at the same time as helium. The output curve for helium was superimposed on the neon curve.

Argon started to come off after 250 cm^3 of carbon dioxide had been passed through, while it was completely removed after 400 cm^3 of carbon dioxide had been used. Krypton started to come off after 425 cm^3, while it finished coming off when 625 cm^3 carbon dioxide had been passed through.

Xenon started to come off after passage of 1800 cm^3 developer, and finished coming off after 2200 cm^3.

One should point out that helium and argon practically moved forward in front of the oven, while krypton and xenon moved with the oven and came off at their characteristic temperatures. The relation between completeness of separation of the rare gases and the amount of material placed on the adsorbent, and the composition of the mixture was studied. Studies showed that even on changing the ratio of the individual components by more than a hundred, there was still good separation of mixtures of helium + neon, argon, krypton, and xenon. Time for a complete analysis was 45 minutes. When 100 cm^3 of a test mixture is used, it is possible to determine the content of the rare gases with an accuracy of up to 0.3%.

A drawback of the chromathermographic method when chromathermograph No. 4 is used, is the fact that when nitrogen is present in a test sample, argon is fixed at the same time as nitrogen. Accordingly, we carried out separations of rare gases on chromathermograph No. 5. The presence of nitrogen did not interfere with argon fixation, since the thermal conductivity of argon differs from that of nitrogen.

Fig. 5 shows an output curve for helium, argon, krypton, and xenon for developer velocities of (v) = 60 cm^3/minute, and rate at which the oven is moved forward (w)= 3.8 cm/minute, and a maximum temperature for the

TABLE 3

Chromathermograph No. 4; Charcoal KAD, 94 g; V_{CO_2} = 40 cm³/minute

Experiment number	Composition of the gas mixture	Volume of developer used before gas starts to come off, in cm³	Volume of developer used to complete elution of gas in cm³	Amount taken in cm³	Amount found in cm³
1	Helium	80	360	7.6	7.7
2	Helium	80	280	6.8	6.8
	Air	300	440		
3	Helium	60	260	12.1	12.0
	Air	280	500		
4	Helium	80	200	22.2	22.3
	Air	220	620		
	Krypton	880	1260		
5	Argon	300	620	7.2	7.2
6	Argon	300	500	6.5	6.4
	Krypton	880	1260		
7	Argon	300	600	14.9	14.8
	Krypton	880	1300		

TABLE 4

Chromathermograph No. 4: Charcoal KAD 94 g: V_{CO_2} = 50 cm³/minute; w = 3.0 cm/minute

Experiment number	Composition of the gas mixture	Volume of developer used before gas starts to come off in cm³	Volume of developer used to complete elution of gas in cm³	Amount taken in cm³	Amount found in cm³	Observations
1	Air	225	400	4.0	4.1	t_{max} = 150°
	Krypton	425	650			
2	Air	225	375	4.0	4.0	Ditto
	Krypton	425	650			
3	Air	200	400	10.0	9.9	Ditto
	Krypton	400	650			
4	Air	150	400	100.0	100.2	t_{max} = 270°
	Krypton	400	675			
	Xenon	1500	2700			
5	Air	175	350	10.3	10.6	Ditto
	Krypton	375	575			
	Xenon	1550	2600			

TABLE 5

Chromathermograph No. 5; Charcoal KAD, 94 g; v_{air} = 60 cm³/minute; w = 3.8 cm³/minute; t_{max} = 205°

Experiment number	Composition of the gas mixture	Volume of developer used before gas starts to come off, in cm³	Volume of developer used to complete elution of gas in cm³
1	Helium	90	270
	Argon	300	600
	Krypton	1170	1710
	Xenon	1890	2220
2	Helium	90	270
	Argon	300	540
	Krypton	1170	1710
	Xenon	1890	2160

oven (t_{max}) = 205°. We see that complete separation of components occurs and that the results are reproducible. Results of chromathermographic separation of rare gases are given in Tables 3,4, and 5. It was shown earlier [8] that on carrying out chromathermographic analysis at a constant temperature for the electric oven, and a constant rate for the forward movement of oven and developer, there is a strict relationship between the heights of the maxima on the output curve and initial concentration. By placing various concentrations of individual components under strictly defined conditions, and measuring concentrations at the maxima of the output curves, we constructed calibration curves relating concentration at the maximum of the output curve to initial concentration.

Numerous experiments showed that using a chromathermographic technique, it is possible to determine concentrations of rare gases in mixtures with an accuracy of up to 0.1%. An analysis takes 45 minutes.

It should be noted that the accuracy of determination of the heavy rare gases can be increased considerably by using a large amount of test material. E.g. an initial concentration of xenon of 0.001%. After passing 20 liters of gas, the concentration on the maximum of the output curve became equal to 1.3%. We call the ratio between the concentration at the maximum of the output curve and the initial concentration the "enrichment coefficient". In the instance quoted this was equal to 1300.

Thus, using a chromathermographic method, we detected heavy rare gases at concentrations of 0.001%.

SUMMARY

1. A chromathermographic method is described for the analysis of hydrogen, carbon monoxide, and methane, at room temperature. 0.1 cm³ of test material is required for an analysis, which takes 30 minutes to carry out, and whose accuracy is 0.3%. This method permits determination of the components indicated when mixed with air.

2. A chromathermographic method is described for the separation and analysis of rare gases. The method permits determination of total helium + neon, argon, krypton, and xenon with great accuracy. On using chromathermograph No. 4, accuracy of determination is 0.3%. When chromathermograph No. 5 is used, accuracy of determination for helium is 0.01% and for the heavy inert gases it is up to 0.001%.

Received May 26, 1955

LITERATURE CITED

[1] A. A. Turkeltaub and N. M. Turkeltaub, Proc. Acad. Sci. USSR, 94, No. 1 (1954).

[2] J. Janak Chem. Listy, 47, 1476 (1953).

[3] N. M. Turkeltaub, V. P. Shvartsman, T. V. Georgievskaya, O. V. Zolotareva and A. I. Karymova, J. Phys. Chem., 27, 12 1827 (1953).

[4] P. Shuftan "Gas Analysis in Technics", State Sci. Tech. Press Ukraine, 1933.

[5] D. A. Vyakhirev, A. N. Bruk, and S. A. Guglina, Proc. Acad. Sci. USSR, 90, No. 4 (1953).

[6] J. Janak, Collected Works of Czechoslovak Chemistry, 19, 684 (1954).

[7] A. A. Zhukhovitsky, O. V. Zolotareva, V. A. Sokolov and N. M. Turkeltaub, Proc. Acad. Sci. USSR 77 3 (1951).

[8] A. A. Zhukhovitsky, N. M. Turkeltaub, and T. V. Georgievskaya, Proc. Acad. Sci. USSR, 92, No. 5 (1953).

BLANK
PAGE

PRECIPITATION CHROMATOGRAPHY IN QUANTITATIVE ANALYSIS

V. D. Kopylova, K. M. Olshanova, and K. V. Chmutov

Institute of Physical Chemistry, Acad. Sci. USSR, Moscow

The question of the relation between the length of a chromatogram zone and the amount of adsorbed material fixed in this zone, was first posed by M. S. Tsvet [1]. Tsvet notes that in such cases there cannot be a proportionality, since the degree of saturation in the colored zones is uneven along the length of the chromatogram. Schwab and Dattler [2], showed that in ion-exchange chromatography, there is only an approximate relation between zone length and the amount of sorbed material, while the zone length depends not only on the concentration of the cation, but on the anion which accompanies it. This phenomenon was also observed by Olshanova and Chmutov [3], during development of sorbed arsenic, antimony, and tin cations with gaseous hydrogen sulfide.

E. N. Gapon and T. B. Gapon [4], while making a study of the given relationship in ion-exchange chromatography, came to the conclusion that the zone length is approximately proportional to the concentration of the ion in the original solution. This relation can only be quantitative with respect to an ion, which is adsorbed to a considerably greater extent than the other ions. In a review article [5], Ryabchikov and Senyavin also denied the possibility of an exact quantitative determination of ions in chromatography on the basis of measurements of zone length, both in the case of a concave, and in the case of a convex sorption isotherm for ion-exchange and molecular chromatography.

Precipitation chromatography is one of the forms of chromatographic analysis which is a method of separating materials based on differences in solubility of sparingly soluble precipitates [6, 7]. A characteristic feature of precipitation chromatography is the clear cut zone boundaries and equal intensity of color along the length of the zone, which testifies to uniform density of precipitate along the length of the zone. This is not observed when other forms of chromatography are used. This characteristic of precipitation chromatography has given many authors the idea of using it for a quantitative analysis of ions [7].

We have made a study of the relation between zone length and concentration of the precipitated ion, using iron, cobalt, and manganese cations as examples.

Through a column consisting of 9 parts by weight of aluminum oxide and 1 part by weight alkali precipitant, was filtered equal volumes (0.5 ml) of solutions of various concentrations of test element nitrates. When this was done, zones whose color intensity was uniform along the zone length, and which had even boundaries were formed. Results of these tests are given in Table 1.

TABLE 1

Solution	Zone length in mm				
	0.5 N	0.25 N	0.125 N	0.625 N	0.0317 N
Fe^{3+}	11	7	4.5	2.5	1
Co^{2+}	12.5	8	5	3	–
Mn^{2+}	12	7	4.5	2	–

Experiments showed that zone length decreased with decreasing cation concentration in solution. It should be noted that the zone length for the same concentration of the various cations was approximately equal, despite the large differences in the solubility product of the precipitates. On the basis of these tests it was shown that it is possible to carry out quantitative determinations of ionic concentrations on the basis of zone lengthsin the chromatogram.

Quantitative Determination of Fe^{3+} Cations in Solution by Means of Precipitation Chromatography

We first of all carried out some tests to find the most suitable carrier and developer, and their relative amounts in the mixture. The following materials were tested as potential carriers: silica gel, kaolin, talc, bleached clay, and anhydrous aluminum oxide. Test showed that kaolin and talc pass the solution through only with difficulty and cannot be used. In the case of silica gel, filtration is fairly rapid, but the lower zone boundaries are very diffuse. Clay gives zones with clearly defined boundaries but the color is uneven.

Aluminum oxide proved to be the best carrier; it gives a homogeneously colored zone with clearly defined and uniform boundaries. Filtration took about 5-7 minutes when a dry column was used. $K_4Fe(CN)_6$ and caustic alkali were tried as precipitants. The first reagent proved to be the most suitable as it was the most sensitive.

TABLE 2

Normality of solution	Neutral solution	0.1 N	0.2 N	0.3 N	0.4 N
Zone length in mm	26	33	38	41	44

TABLE 3

1 ml of solution + + 2 drops of 2N Acid	HCl	H_2SO_4	HNO_3
Zone length in mm	35	38	40

We found out experimentally that the optimum ratio of carrier to precipitant was 100 : 1. The precipitant was introduced as a solution in order to get a uniform distribution. 5 ml of a 1 N solution of $K_4Fe(CN)_6$ was mixed with 50 g of aluminum oxide, which was then ready for use.

When choosing the ratio between carrier and precipitant the following regularities were observed: zone length for the same concentration of precipitated cation, but for different amounts of precipitant, was identical, though the intensity of the zone color decreased appreciably with decreasing amount of precipitant. Experiments were carried out on the influence of hydrogen ion concentration on zone length. Results of these experiments are tabulated in Table 2. Experimental results showed that with decreasing pH of the solution, for one and the same Fe^{3+} concentration, the zone length increased. It may be postulated that at high hydrogen ion concentrations, partial solution of precipitate may occur; moreover, hydrogen ions on being adsorbed, lower the adsorption of test ion, which may lead to an increase in zone length. The lower boundary of the zone was somewhat diffuse. The difference in precipitate solubility in different acids also affects zone length (Table 3).

Experiments showed that different acids, fat equal concentrations, affect zone length to different degrees. The precipitate is most soluble in nitric acid.

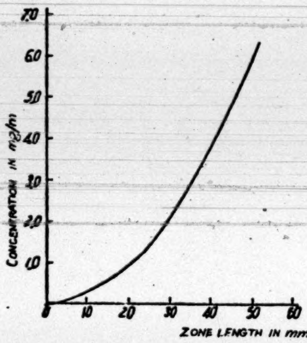


Fig. 1. Relation between zone length and Fe^{3+} concentration.

When Fe^{3+} concentration is being determined by means of precipitation chromatography, it is essential to neutralize any free acid beforehand. Neutralization is carried through to the point where the first sign of turbidity as a result of precipitate formation is observed; one drop of 2 N hydrochloric acid is then added to remove the turbidity.

A calibration curve was constructed on the basis of the results obtained; this curve related zone length to concentration of the cation in the same volume of solution as that taken for test. Zone length in mm was plotted along the abscissa and Fe^{3+} concentration in mg/ml along the ordinate.

On the basis of these experiments a method has been worked out for the determination of Fe^{3+} by means of precipitation chromatography.

a) Preparation of column: carrier — anhydrous aluminum oxide is carefully mixed with 1 N solution of precipitant, in the ratio of 5 ml of 1 N $K_4Fe(CN)_6$ per 50 g aluminum oxide. This mixture is placed in a column 4 mm in diameter and 12-15 cm long; the height of the prepared column is 5-6 mm. The column is packed by tapping it on a hard surface until the volume does not change any further. Before doing a run, another 2-3 drops of 0.5 N precipitant solution is added to the column.

TABLE 4

Experiment number	Zone length in mm				Concentration in mg/ml	
	1	2	3	Mean	From the graph	Gravimetrically
1	7.0	7.5	7.0	7.0	0.28	0.21
2	10.5	10.5	10.5	10.5	0.38	0.32
3	12.0	12.0	12.0	12.0	0.45	0.47
4	13.5	13.5	13.5	13.5	0.52	0.52
5	17.0	17.0	17.0	17.0	0.72	0.68
6	20.5	20.5	20.5	20.5	0.96	0.87
7	27.0	26.5	27.0	27.0	1.64	1.55
8	29.0	29.0	28.5	29.0	1.84	1.90

b) Determination of Fe^{3+} in solution is carried out as follows: 1 ml of neutralized test solution is introduced into the column. When filtration is complete, zone length is measured and iron concentration then determined from the graph. Table 4 contains results of determinations which are compared with results obtained by a gravimetric technique. Deviation between the gravimetric and chromatographic methods was not more than 4%. This method is therefore suitable in those cases where a particularly high degree of accuracy is not required. The method could be used for determining iron concentration in the presence of other ions when the concentration of the latter is constant.

The method possesses the following advantages:

1) an analysis takes 15-20 minutes, including preparation of a column. Filtration which takes 10-15 minutes, requires no attention from the analyst;

2) only ca. 4 ml of solution is necessary.

3) experimental technique is simple and may be carried out under field conditions.

SUMMARY

It has been demonstrated that it is possible to determine iron quantitatively in the absence of other cations, by means of precipitation chromatography, on the basis of the length of the colored zone.

Received August 6, 1954

LITERATURE CITED

[1] M. S. Tsvet, "Chromatographic Adsorption Analysis" 1946.

[2] G. M. Schwab, and G. Dattler. Angew. Chem., 51, 709 (1938).

[3] K. M. Olshanova and K. V. Chmutov, J. Anal. Chem., 11, 94 (1956)(T. p. 93)*

[4] E. N. Gapon and T. B. Gapon. J. Gen. Chem., No. 3, 1627 (1949)(T. p. a-49)*.

[5] D. M. Ryabchikov and M. M. Senyavin. J. Gen. Chem., 23 (1953)

[6] E. N. Gapon and T. B. Gapon. Proc. Acad. Sci. USSR, 60, 401 (1948).

[7] E. N. Gapon and I. M. Belenkaya, Colloid J., 14, 323 (1952)(T. p. 353)*.

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

DETECTION OF TRACES OF NICKEL BY MEANS OF PRECIPITATION CHROMATOGRAPHY

V. V. Olshanova

Lvov Polytechnical Institute

Of reactions described in the literature for the qualitative detection of nickel, the best appears to be that with dimethylglyoxime which was suggested by L. A. Chugaev [1].

This reaction is almost specific for nickel (palladium Pd^{++} also gives a precipitate with dimethylglyoxime) and is very sensitive [2].

All the same, the presence in solution of large amounts of cobalt, iron, or copper [2,3], complicates matters considerably from the point of view of applying this reaction in practice; leads to a decrease in sensitivity; and sometimes completely precludes its application. The root of the trouble is the capacity of the ions Fe^{++}, Co^{++}, Co^{+++}, and Cu^{++} [4-8], to form soluble colored complexes with dimethylglyoxime, on a background of which it is impossible to distinguish small amounts of a precipitate of nickel dimethylglyoxime. The appreciable solubility of the nickel precipitate in solutions of salts of the elements mentioned is also a contributory factor toward getting poor results.

One comes up against difficulties of this nature for example when trying to determine the nickel content of cobalt salts. F. Feigl and G. Kapulitzas [9], in this particular instance, avoided the difficulty by using the difference in stability of the cyanide complexes of trivalent cobalt and divalent nickel. The less stable nickel complex is decomposed with formaldehyde, and the nickel cyanide formed gives the characteristic compound. Nevertheless, since these cyanide compounds are poisonous, it is not very easy or desirable to work with them.

It was of interest therefore to try and use the technique of precipitation chromatography for the analysis of materials containing small amounts (traces) of nickel. The use of such a technique might simplify the problem of detecting as well as determining nickel e.g. in cobalt preparations, and also obviate the use of cyanides.

EXPERIMENTAL

The principle of precipitation chromatography, which was developed by T. B. Gapon and E. N. Gapon [10], can be described as follows. Test solution is passed through a column charged with a suitable filtering material or carrier, to which has been added a precipitant which gives a characteristic precipitate with the test ion. Under these conditions, sparingly soluble compounds are formed by interaction of test ions with precipitant; these separate out in the form of separate zones. The zone sizes characterize, to some extent, the quantitative composition of the test solution. The order in which zones are arranged depends on the value of the solubility product of the precipitate formed, the way in which the chromatogram is prepared, and other factors [11].

Method and Experimental Procedure

Dimethylglyoxime (DMG) was used as precipitant. This precipitant forms a sparingly soluble, highly colored compound, with Ni^{++} only. The solubility product of nickel dimethylglyoxime is $2.2 \cdot 10^{-25}$ [12], one would expect therefore that nickel ions will be retained on a column, while the complex compounds which DMG forms with cobalt, copper, and iron (II), being readily soluble and differing in composition and color, will be readily eluted from the column with water, so that only one zone, that of nickel, will remain on the column.

To find the best carrier, experiments were carried out on $BaCO_3$, ZnO, calcined Al_2O_3 (all reagents were of analytical quality), Al_2O_3 for chromatographic purposes, and glass powder. Columns were also tested which were simply filled with dimethylglyoxime on its own (this reagent was also of analytical quality). In carrying out these tests it was borne in mind that the substances mentioned above (apart from DMG) will impart a slightly alkaline reaction to the solution, and, consequently, will favor the formation of nickel dimethylglyoxime, since the optimum conditions for the formation of this precipitate lie within the pH limits of 5-10 [13].

All the potential absorbents were prepared by triturating dry carrier and precipitant, mixed in various weight ratios, in a porcelain mortar.

The micro columns we used were glass tubes 50-70 mm long, 5-8 mm in diameter, which were drawn on one side into a capillary with a diameter of 1-2 mm. A small bit of glass wool was fitted into the tube to serve as a support for the absorbent layer. Absorbent was introduced into the dry tube and compacted by tamping it gently on a solid surface. The height of the absorbent column formed was 5-10 mm.

Experiments were carried out both with dry and moist columns. Moistened columns were experimentally shown to possess no advantages over dry ones. The only exception were columns filled with DMG alone, which is not readily wetted with neutral solutions; accordingly columns of this type were treated with a drop of NH_4OH (1:1) and 1-2 drops of water before use. The water was necessary to wash the ammonia off the column walls and prevent precipitation of metal hydroxides on them. We noted that treatment of DMG with ammonia favors the formation of nickel dimethylglyoxime.

Experimental Procedure. One drop (or a few) — 0.05 ml — of test solution was introduced into the column prepared; after 2-5 minutes the solution was soaked up by the absorbent, after which the column was washed with 10-20 drops of water, until a colorless filtrate was obtained, when the column was carefully examined. The formation of a zone of nickel dimethylglyoxime with a rose color, which is easily observable on a backgroundof white DMG, showed that the reaction gives positive results.

Detection of Nickel in Solutions of Its Salts

For detection of Ni^{++}, neutral solutions $1 \cdot 10^{-3}$ N with respect to nickel, were prepared from nickel sulfate, chloride and nitrate respectively which were either chemically pure grade or analytical grade. More dilute solutions were prepared by diluting these stock solutions with distilled water.

Experimental results are given in Table 1.

The results given in Table 1 show that Ni^{++} can be detected by means of precipitation chromatography. The best absorbents were shown to be: DMG treated with ammonia; a mixture of 10% DMG + 90% Al_2O_3 used for chromatography; a mixture of 10% DMG + 90% glass powder. Reaction sensitivity was practically identical on these absorbents; the limit of identification was 0.075 μg Ni^{++} in a drop of solution. SO_4^{-}, NO_3^{-}, and Cl^{-} have practically no effect on the sensitivity.

It should be noted that absorption of nickel ions from ammoniacal solutions (NH_4OH concentration should be ca. 0.01 N) on dry columns charged with DMG, leads to similar results.

Detection of Nickel in the Presence of Cobalt

Detection of Ni^{++} in the presence of interfering ions has been studied by many authors [3]. According to Feigl's results [2], it is difficult to detect 0.00003 g of nickel in the presence of a 100-fold excess of cobalt by means of Chugaev's reaction; in the presence of still greater amounts of cobalt, Feigl recommends a special procedure [9]. We used precipitation chromatography for this purpose.

Nickel nitrate and either cobalt chloride or nitrate were used for test. Cobalt salts were prepared from a preparation of $CoCl_2 \cdot 6H_2O$ analytical grade via the purpureo salt — chloropentamminocobaltichloride — according to the procedure described by Perelman, Zvorykina, and Gudima [14]. The final product did not contain any detectable amount of nickel (the product was checked by means of Feigl and Kapulitsas' method [9]). The concentration of stock solutions was checked gravimetrically: nickel — by the dimethylglyoxime method —, and cobalt as the sulfate. By mixing the respective solutions of nickel and cobalt in varying proportions, solutions were obtained with different nickel and cobalt concentrations. The weight ratio of Ni:Co varied from 1:50 to 1:5000. The composition of the absorbents used and the results obtained are given in Tables 2 and 3.

As is evident from the tables, it is possible to separate Ni^{++} and Co^{++} by means of precipitation chromatography. This method allows detection of traces of Ni^{++} in the presence of a 5000 fold amount of Co^{++}, without resorting to the use of potassium cyanide. The best results were obtained on the following absorbents: 1) DMG, treated with ammonia; 2) 10% DMG + 90% glass powder. Reaction sensitivity depends on the ratio of Ni:Co and on absorbent composition; sensitivity decreases with a decreasing ratio of Ni to Co. The poor sensitivity of the reaction (bad separation) on columns of DMG + Al_2O_3 (special for chromatography), can probably be explained by the fact that in the given instance of the pair $Ni^{++}-Co^{++}$, a mixed zone is formed, since the chromatographic properties of the aluminum oxide come into play in this case.

TABLE 1

Detection of Ni^{++} by means of Precipitation Chromatography

Experiment number	Absorption composition	Nickel concentration in solution			
		$1 \cdot 10^{-3}$ N	$1 \cdot 10^{-4}$ N	$5 \cdot 10^{-5}$ N	$2.5 \cdot 10^{-6}$ N
1	DMG. treated with ammonia	+	+	+	−
2	10% DMG + 90% $BaCO_3$	+	+	−	−
3	10% DMG + 90% ZnO	+	Unreliable	−	−
4	10% DMG + 90% Al_2O_3 (calcined)	+	+	−	−
5	10% DMG + 50% Al_2O_3 (calcined	+	Unreliable	−	−
6	10% DMG + 90% Al_2O_3 (special for chromatography)	+	+	+	+*
7	50% DMG + 50% Al_2O_3 (special for chromatography)	+	+	Unreliable	−
8	10% DMG + 90% glass powder	+	+	+	−
9	50% DMG + 50% glass powder	+	+	Unreliable	−

---

* 2 drops of nickel salt solution were taken.

TABLE 2

Detection of Nickel in the Presence of Large Amounts of Cobalt (in all tests the nickel concentration of the solution was $1 \cdot 10^{-3}$)

Experiment number	Absorbent composition	Weight ratio of Ni : Co					
		1 : 50	1 : 100	1 : 200	1 : 500	1 : 1000	1 : 5000
1	DMG treated with ammonia	+	+	+	+	+	+
2	10% DMG + 90% Al_2O_3 (special for chromatography)	+	+	Unreliable	−	−	−
3	50% DMG + 50% Al_2O_3 (special for chromatography)	+	+	+	Unreliable	−	−
4	10% DMG + 90% glass powder	+	+	+	+	+	+
5	50% DMG + 50% glass powder	+	+	+	+	Unreliable	−

TABLE 3

Sensitivity of the Reaction for Ni^{++} in μg of Nickel in a Drop of Solution for Various Ratios of Ni : Co

Experiment number	Absorbent composition	Weight ratio of Ni : Co					
		1 : 50	1 : 100	1 : 500	1 : 1000	1 : 3000	1 : 5000
1	DMG treated with ammonia	0.125	0.25	0.25	0.40	0.50	0.50
2	10% DMG + 90% Al_2O_3 (special for chromatography)	1.0	1.5	Not determined			
3	50% DMG + 50% Al_2O_3 (special for chromatography)	0.5	0.5	1.5	Not determined		
4	10% DMG + 90% glass powder	0.15	0.25	0.4	0.5	−	1.0
5	50% DMG + 50% glass powder	−	0.5	−	1.5	−	−

TABLE 4

Specification	Permitted amount of nickel in the preparation GOST* 4528-48	Ratio of Ni : Co in the preparation	Sensitivity: Ni^{++} in a drop of solution in μg	Weight of aliquot
Pure	0.5	1:40	0.125	0.005
Analytical grade	0.05	1:400	0.25	0.10
Chemically pure	0.02	1:1000	0.40	0.40
Nickel free	<0.005	1:4000	0.50	2.00

---

* All-Union State Standard.

The experimental results obtained (Table 3), in conjunction with the spot method proposed by Shemyakin and Mitselovsky [16] for the quantitative determination of ions, can can be used for determining the purity of cobalt preparations by the method of precipitation chromatography. For this purpose, in accordance with GOST*[15], it is necessary to prepare solutions of the test preparations so that the Ni^{++} concentration in them is the minimum which can be detected for a given ratio of Ni : Co. Calculation of the weight of the preparation can be carried out by means of the formula:

$$W = \frac{V \cdot K \cdot S}{\% \cdot 10{,}000}\ g$$

where W – is the weight of the preparation in g; V – the volume of solution prepared in ml; K – the number of drops in ml; S – sensitivity of the reaction in micrograms of nickel in a drop of solution, for a given ratio of Ni : Co; % – the permissible % of nickel in the preparation according to GOST* ; 10,000 – conversion factor.

As an example we give the weight of $Co(NO_3)_2 \cdot 6H_2O$ calculated according to this formula (it is assumed that: the volume of solution V = 10 ml; and K = 20 drops in a ml; the reaction sensitivity is taken from the results given in Table 4 for dimethylglyoxime as the absorbent).

Solutions prepared so as to contain such weights of nickel, were tested on columns charged with DMG, using the method described above; results of tests on two mixtures of them were compared. When a solution (one drop) prepared from the biggest weight gave a positive reaction, while the solution prepared from the smallest gave a negative reaction, this meant that the preparation agreed with specification corresponding to the smallest weight.

This technique could, in our opinion, be used for inter-factory control of the purity of cobalt preparations with respect to nickel or for checking its grade (mark).

Detection of Nickel in the Presence of Iron

Detection of traces of nickel in the presence of Fe^{+++} and Fe^{++} by the usual method is impossible, since Fe^{+++} forms a colored precipitate in ammoniacal solution, while Fe^{++}, in the presence of DMG forms a soluble complex with a carmine-red color [4, 5, 8].

Interference from Fe^{+++} can be inhibited by using masking agents. To inhibit the effect of Fe^{++}, it is first oxidized to Fe^{+++}, and then a masking agent is used as before. We used precipitation chromatography for detecting nickel in the presence of ferrous and ferric iron.

Tests showed that in this case it is expedient to use complexing agents which form complexes with iron which are stable in ammoniacal media.

Experiments were carried out with Mohr's salt to which had been added nickel nitrate and sufficient Seignette salt (potassium sodium tartrate) to complex the iron. The acid formed by the interaction of iron with the tartrate was neutralized with ammonia (1 : 1), and the pH adjusted to 8-10. At lower pH values, these solutions are unstable and a precipitate settles out, probably precipitates of basic iron salts, while at higher pH's, reaction sensitivity for nickel drops. The ratio Ni : Fe was varied from 1 : 10 to 1 : 2300. Chromatograms were obtained on columns charged with DMG (dry) and a mixture of 10% DMG + 90% glass powder. No other absorbents were used.

It was established experimentally that 0.15 μg of Ni^{++} can be reliably detected on both absorbents in the presence of a 2300-fold amount of iron (II). Solutions with higher ratios of Ni : Fe were not tested.

Detection of Nickel in the Presence of Copper

Copper ions Cu^{++}, form stable complexes with DMG, as Babko and Korotun showed [6]. Formation of these compounds has a deleterious effect on the sensitivity of the Chugaev reaction if it is carried out in the presence of Cu^{++} [3].

In order to diminish the effect of Cu^{++}, we used chromatographic separation of the pair Ni^{++}–Cu^{++}, using this process at the same time for detecting small amounts of Ni^{++} in the presence of large amounts of copper.

It was found that the best way to separate this pair of metals was to chromatograph nickel and copper ions from solutions of their complex compounds with ammonia or tartrate at a pH of ca. 7-8. On passing solutions whose pH is appreciably greater than the value indicated through a column filled with DMG, a black colored zone is formed which might indicate formation of copper dimethylglyoxime to some extent. This zone is destroyed on eluting the column with water. Sometimes the nickel zone is also destroyed at the same time as the copper zone; accordingly detection of Ni^{++} at high pH's is impossible.

---

* All-Union State Standard.

In our experiments we used solutions of cupric sulfate to which the respective amounts of nickel salts had been added. The solutions also contained sufficient NH_4OH + NH_4Cl (the latter is used to lower the pH) or sodium tartrate to complex all the nickel and copper. The ratio Ni : Cu was varied from 1 : 10 to 1 : 2000. Experiments were carried out with columns filled with DMG treated with ammonia, or a mixture of 10% DMG + 90% glass powder. It was found that 0.25 μg of Ni^{++} in a drop of solution can be detected in the presence of 2000 times its amount of copper.

SUMMARY

1. It has been shown that it is possible to detect small amounts (traces) of nickel in the presence of large amounts of cobalt, iron, and copper.

2. It has been established that the sensitivity of the Chugaev reaction for nickel decreases on decreasing the ratio Ni : Co (Fe, Cu). Thus, in solutions of nickel salts, the limit of identification is equal to 0.075 μg Ni^{++} in a drop, for ratios of Ni : Co = 1 : 50-0.125 μg, while for a ratio of Ni : Co = 1 : 5000 it is only 0.5 μg of dimethylglyoxime as the absorbent. SO_4^{--}, NO_3^{-}, and Cl^{-} have practically no effect on reaction sensitivity.

3. The best absorbents found from those tested were shown to be: 1) dimethylglyoxime treated with ammonia; 2) a mixture of 10% dimethylglyoxime and 90% glass powder.

The absorbent composed of dimethylglyoxime and special aluminum oxide for chromatography did not ensure separation of the tested pairs of ions.

4. It has been established that complex formation with ammonia and tartrate respectively, has a positive effect on the separation of $Ni^{++}-Co^{++}$, $Ni^{++}-Fe^{++}$, and $Ni^{++}-Cu^{++}$.

5. A method has been worked out for detecting traces of nickel in cobalt salts without having to resort to potassium cyanide and a simple procedure is suggested for testing the specification of cobalt preparations with respect to nickel.

Received October 25, 1954

LITERATURE CITED

[1] L. A. Chugaev, J. Russ. Phys. Chem. Soc., 37, 243 (1905).

[2] F. Feigl, "Spot Analysis", State Chem. Press Moscow-Leningrad 1933, p. 165 et al.

[3] "Reactions and Reagents for the Qualitative Analysis of Inorganic Compounds", Edited by A. S. Komarovsky, Moscow-Leningrad, 1950, p. 464.

[4] L. A. Chugaev, "Selected Works", Vol. 1, USSR Acad. Sci. Press, Moscow 1954, pp. 75-77.

[5] L. A. Chugaev, "Selected Works", Vol. 1 USSR Acad.Sci. Press, pp. 464-466 (in conjunction with V. P. Orelkin).

[6] A. K. Babko and M. V. Korotun, J. Gen. Chem., 23, 1302 (1953) (T. p. 1367)*.

[7] A. K. Babko and M. V. Korotun, J. Gen. Chem., 24, 597 (1954) (T. p. 609)*.

[8] A. K. Babko and L. I. Dubovenko, J. Gen. Chem., 24, 751 (1954) (T. p. 759)*.

[9] F. Feigl and H. J. Kapulitzas, Z. anal. Chem., 82, 417 (1930); cited in F. Feigl "Spot Analysis", 1933.

[10] T. B. Gapon and E. N. Gapon, Proc. Acad. Sci., 60, 401 (1948).

[11] E. N. Gapon and I. M. Belenkaya, Colloid J., 14, 323 (1952) (T. p.)*.

[12] A. K. Babko and P. B. Mikhelson, Trans. Commission on Anal. Chem., Vol. 8, pp. 61-67, 1954.

[13] V. N. Alekseev, "A Course of Qualitative Chemical Semi-micro Analysis", State Chem. Press, Moscow-Leningrad, 1952, p. 278.

[14] F. M. Perelman, A. Ya. Zvorykin, and N. V. Gudima, "Cobalt", USSR Acad. Sci. Press, Moscow, 1949, pp. 150-151.

---

* T. p. = C. B. Translation pagination.

[15] Inorganic Reagents. Collection of Standards, Part II, Standard State Press, 1949, pp. 121-139.

[16] F. M. Shemyakin and E. S. Mitselovsky. Author's Thesis No. 87279 cited from "References to Reports Presented at the Conference on Chromatography", USSR Acad. Sci. Press, 1950, p. 186.

A METHOD FOR THE ANALYSIS OF VANADIUM CARBIDES

M. A. Gurevich, B. F. Ormont, and M. Z. Nokhimovskaya

The L. Ya. Karpov Institute of Physical Chemistry

A large amount of work has been published on the synthesis and structure of vanadium carbides. Unfortunately, in most of the papers published, analytical results are not given [1-6], or are simply given without any indication of the analytical methods used, which leaves one in doubt as to their reliability [7-15]. Only a few articles contain brief information on the essentials of the methods used [16-18].

Determination of free carbon in vanadium carbides was carried out by Morett [18], 1938, who dissolved the carbides in nitric acid of unknown concentration at a temperature which is also not given. The undissolved free carbon was determined, like total carbon, gravimetrically. Vanadium was determined either gravimetrically [17] — by calcining the carbide in a stream of oxygen and weighing the V_2O_5 formed —, or volumetrically [16-18]. — by titration with potassium permanganate.

Determination of Vanadium

We established in the course of our work that on carrying out a combustion of vanadium carbide in a boat, the vanadium pentoxide (melting point ca. 715°) formed, under the influence of capillary forces, wets the boat walls and is distributed along the tube walls in a Mars oven: this presumably is the source of the large errors obtained on weighing.

We eliminated this source of error by placing finely ground annealed quartz powder in the boat. The liquid V_2O_5 formed then wets the surface of the quartz powder and is completely held by the boat.

In order to determine the conversion factor it was necessary to check on the correspondence between the composition of the combustion product of vanadium carbide — and the stoichiometric composition for the pentoxide, i.e. V_2O_5.

In order to determine the best conditions for combustion, an aliquot of carbide was subjected to a series of successive calcinings in an oxygen stream, each time for 3 hours, at temperatures of 600, 800, 950, and 1100°. The results obtained for one of the samples are given in Table 1.

TABLE 1

Combustion temperature in °C	Total carbon content C_{total} in %	Vanadium content V in %	Increase or decrease after each successive combustion	
			C_{total} in %	V in %
600	12.73	81.55	—	
800	14.00	83.43	+ 1.27	+ 1.88
950	14.76	83.60	+ 0.76	+ 0.17
1100	14.93	83.00	+ 0.15	−0.60

It is clear from Table 1 that when combustion is carried out at 600, 800, and 950°, there is an increase in oxygen (the calculated vanadium content in % increases). Increasing the temperature to 1100° with subsequent calcining for 3 hours leads to a loss of oxide, as a result of partial decomposition. Consequently, the calculated vanadium content drops. The optimum temperature for combustion therefore appears to be 950° in the case of vanadium determination.

Determination of Total Carbon

We determined total carbon by means of a method developed by Smirnova and Ormont [19, 20]: this consisted in trapping the gases from the combustion of vanadium carbide in a specially constructed absorbing scrubber, which ensured complete adsorption of CO_2 by standard $Ba(OH)_2$ solution; excess $Ba(OH)_2$ was titrated with hydrochloric acid.

It is clear from Table 1 that calcining at 1100° allows one to trap additional amounts of CO_2. It is clear that, in contrast to Ta_2O_5, liquid vanadium pentoxide coats the preparation, and prevents the carbon from being completely burnt.

TABLE 2

Sample	Chemical composition in %			
	C_{total}	C_{free}	V	Total V + C_{total}
104	6.97		92.20	99.17
104	6.70		92.00	98.70
				98.94 ± 0.24
64	12.20	1.09	84.50	96.70
64	12.02	–	84.54	96.56
				96.63 ± 0.07
108	14.00	1.65	84.50	98.50
108	13.46	1.80	84.65	98.11
				98.30 ± 0.20
105	14.60	0.07	84.10	98.70
105	14.28	0.07	84.00	98.28
				98.49 ± 0.21

Other difficulties were observed when vanadium carbides were calcined. Vanadium carbides often ignite in oxygen and explode; accordingly it is essential to ensure that the temperature is only taken up slowly, and that the tube containing the boat be moved very slowly into the hot part of the oven. As a consequence of this type of combustion, it is necessary, in order to prevent CO getting through, to use cupric oxide, which we placed at the end of the combustion tube, or in a separate oven next to the oven used for combustion.

Determination of Free Carbon

We standardized the conditions for dissolving vanadium carbides in nitric acid, and found that the best solvent mixture is one consisting of nitric acid and water in a ratio of 2: 1. To carry out an analysis, ca. 200-300 mg of carbide was placed in a beaker containing 50-100 ml of the acid with the concentration indicated; the sample was then dissolved by heating to the boil over a gas flame. Under these conditions, the carbides dissolved in a few minutes. Prolonged boiling is not advisable in case hydrolysis products separate out.

The undissolved free carbon was filtered through a quartz tube fitted with a quartz porous filter (or through a Gooch asbestos crucible).

After the precipitate of carbon had been washed together with the quartz filter (or with the asbestos from the Gooch crucible), the whole was transferred to a Mars oven and combustion was then carried out followed by volumetric determination according to the method described above. If it is necessary, a micro-method described previously can be used [19].

Below we have given as an example, in Table 2, analytical results for several samples of carbides (oxygen was determined by difference).

Obtaining a high accuracy, particularly with relation to the determination of total carbon, is made difficult for the reasons mentioned above.

Breaking up the sample followed by repeated combustion sometimes improved the results to some extent.

SUMMARY

Vanadium has been determined in carbide gravimetrically. The optimum combustion temperature is 950°. Finely ground annealed quartz is placed in the boat used for combustion to prevent wetting of the boat and tube walls by vanadium pentoxide.

Total carbon was determined volumetrically – by absorption of CO_2 with standard $Ba(OH)_2$ followed by back titration of excess $Ba(OH)_2$ with hydrochloric acid.

Free carbon was determined by dissolving the carbide in a 2: 1 mixture of nitric acid and water, on heating the mixture to the boil. Insoluble free carbon was determined by the volumetric method described for total carbon.

Received May 25, 1955

LITERATURE CITED

[1] K. Becker. and F. Ebert. Z. Phys.. 31. 268 (1925).

[2] C. Agte. and K. Moers. Z. anorg. allg. Chem., 198, 233 (1931).

[3] S. E. Oldham. and W. P. Fishel. J. Am. Chem. Soc., 54, 3610 (1932).

[4] T. Hanawalt. H. Rinn. and L. Frevel. Ind. Eng. Chem., No. 9 (1938).

[5] E. Maurer. T. Doring and W. Pulewka, Arch. Eisenhüttenwes. 13, No. 8, 337 (1940).

[6] T. Norton, and A. L. Mowry. J. of Metals (Technology—Practice) 1, No. 2 (1949).

[7] Henry Moissan. Comptes rend.,116, 1225 (1893).

[8] Henry Moissan, Comptes rend., 122, 1297 (1896).

[9] Paul Pütz, Metallurgie, 3, No. 18-20, 635, 649, 677 (1906).

[10] O. Ruff. W. Martin, Z. angew. Chem and Zentr. techn. Chem., 25, No. 2, 49 (1912).

[11] E. Maurer, Stahl and Eisen, 45, No. 39, 1629 (1925).

[12] A. Osawa. and M. Oya. Sci. Rep. Tokyo Imp. Univ., 19, 95 (1930).

[13] W. Dawihl. and W. Rix. Z. anorg. allg. Chem., 244, No. 2, 191 (1940).

[14] H. Krainer, and K. Conopicky. Berg- and Hüttenmann Monatsh. Montan Hochschule Leoben, 92, 166 (1947).

[15] H. Krainer, Arch. Eisenhüttenwes. 21, 1/2, 33 and 39 (1950).

[16] T. O. Arnold. and A. A. Read. J. Iron and Steel Inst., 5, 35, No. 1, 215 (1912).

[17] E. Friederich, and L. Sittig. Z. anorg. allg. Chem., 144, 169 (1925).

[18] A. Morett. Bull Soc. chim. 5, 1063 (1938).

[19] V. I. Smirnova and B. F. Ormont, J. Anal. Chem., 9, 359 (1954) (T. p. 399)*.

[20] B. F. Ormont and V. I. Smirnova, J. Anal. Chem., 9, 364 (1954) (T. p. 405)*.

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

DERIVATIVES OF RHODANINE AND 2-THIOHYDANTOIN AS REAGENTS FOR INORGANIC ANALYSIS

N. M. Turkevich and V. F. Gevlich

State Institute of Medicine at Lvov

Derivatives of rhodanine and 2-thiohydantoin have been carefully studied by Dubsky [1,2], and Feigl [3, 4], and on the basis of their work p-dimethylaminobenzylidenerhodanine and p-dimethylaminobenzylidenethiohydantoin have been introduced into analytical practice as sensitive reagents.

Dubsky, on the basis of his studies, assumed that the functional-analytical group for silver is the group of atoms $S=\overset{|}{C}-NH-\overset{|}{C}=$, which occurs in the molecules of the materials just indicated. According to Kulberg [5], silver can replace hydrogen to form the group $S=\overset{|}{C}-NAg-\overset{|}{C}=$; Voznesensky [6], also assumed that in the molecule of the compound with silver, the group $S=\overset{|}{C}-NAg-\overset{|}{C}=$ and $AgS-\overset{|}{C}=N-\overset{|}{C}=$ is present. The results of our work [7-9], have excluded the existence of this last group ; our results showed that rhodanine is not capable of tautomerization, and that the group $>C=S$ which is present in its molecule, has a typical thioketonic character.

The presence of two primary groups in molecules of silver compounds in which the silver atom is connected directly with nitrogen, is also doubtful, since one of us [10], has shown that 3-substituted derivatives of rhodanine* are also sensitive reagents for silver, and are capable of precipitating this element from solutions of silver nitrate. The silver compounds obtained [11], appear to be complex compounds in whose molecules there is combined silver nitrate. Similar results were obtained with mercury salts.

Salt formation during interaction of silver inorganic salts with certain rhodanine derivatives, is indicated by elemental analysis of silver compounds obtained during such interactions, by Nencki [16], and Dubsky [1]. It should be noted however that this position does not extend to all 5-substituted rhodanine derivatives, irrespective of the nature of the substituent, and even more so in the case of 3-substituted derivatives. The fact that unsubstituted rhodanine forms a typical complex compound with copper chloride also testifies to this [1].

We made a careful study of the reactions which occur between many derivatives of rhodanine and 2-thiohydantoin respectively, and various ions. For this purpose we prepared aqueous solutions of the salts of uni- and divalent copper, rubidium, trivalent gold, uni- and divalent mercury, silver, beryllium, zinc, strontium, cadmium, barium, di- and tri-valent iron, aluminum, lanthanum, univalent thallium, trivalent arsenic, titanium, zirconium, divalent tin, lead, trivalent antimony, tri- and quinquevalent vanadium, bismuth, trivalent chromium, sexivalent tungsten, manganese, cobalt, nickel palladium, quadrivalent platinum, tri- and quadrivalent cerium, sexivalent uranium, and quadrivalent thorium. Organic reagents were prepared as a 0.2% alcoholic solution; to one drop of such a solution was added one drop containing 0.5 mg of the test ion. In addition, in a separate test, 1 drop of 10% ammonia solution was added.

The present article contains results obtained with 8 organic reagents which included 3-substituted rhodanine derivatives, and 4- substituted derivatives of 2-thiohydantoin. The tests we carried out, indicate new possibilities for the use of the reagents indicated, and also, to some extent, indicate the mechanism of the reactions which occur.

Rhodanine and its Derivatives

Rhodanine (I) forms solutions with a yellow-green tint which intensifies on addition of ammonia; it gives characteristic reactions with many cations (Table 1 ; the elements in brackets are those which react in ammoniacal

---

* A number of rhodanine derivatives which Kulberg et al. claimed to have synthesized for the first time, had already been described in the articles of N. M. Turkevich and coworkers [11], Gendelman [12], Granacher and coworkers [13], Bargellini [14], Zipser [15], and others.

TABLE 1

Characteristic Reactions of Rhodanine and its Derivatives

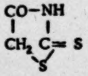
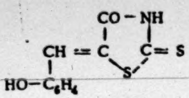
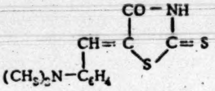
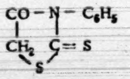
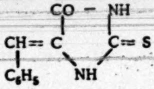
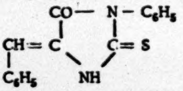
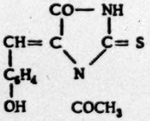
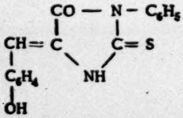
Reagents	Colors	Ions
 (I)	orange	Cu^{I}, Au, Fe^{III}, Pt, Sb (Mn, Ni)
	yellow	Hg^{I}, Hg^{II}, Ag, Tl, Pb, V^{III}, V^{V}, U, Pd (Ag)
	brown	Cu^{II}, Ce^{IV}, (Bi, Cu^{I}).
	violet	(Co)
 (II)	cherry-red	Cu^{II} (Cu^{I}, Cu^{II}, Hg^{I}, Hg^{II}, Ag, Tl).
	orange	Au, Hg^{I}, Ag, Al, V^{V}, Ni, Pd, Pt
	brown	Tl, Hg^{II}, Pb, V^{III}
 (III)	cherry-red	Cu^{II}, Hg^{II}, Tl, Zr, Pd, Pt, Ag (Cu^{I}, Pd, Ce^{III}).
	violet brown	Au, Hg^{I}
	orange	(Pb, Pt)
 (IV)	yellow	Cu^{I}, Hg^{I}, Hg^{II}, Tl (Hg^{II}).
	cherry-red	(Cu^{I}, Cu^{II}, Hg^{II}, Ag, Au, Fe^{II})
	brown	Cu^{II}, Au, Ag, Pd (Ag, Tl, Ni).
	orange	Pt (Pd)

TABLE 2

Characteristic Reactions of 2-Thiohydantoin Derivatives

Reagents	Colors	Ions
 (V)	yellow	Cu^{I}, Hg^{I}, Hg^{II}, Ag, Pd, Ce^{III}, (Zn)
	orange	Au, Cu^{II}, Pt (Cu^{I}, Cu^{II})
 (VI)	yellow	Cu^{I}, Hg^{I}, Hg^{II}, Ag, Au, Tl (Ag)
	orange	Cu^{II}, Pd, Pt (Cu^{II})
	red	(Cu^{I})
 (VII)	cherry-red	Au, Tl (Cu^{II})
	orange	Hg^{I}, W, Pd, Pt (Zn)
	yellow	Ag, Hg^{II}
	brown	Cu^{II}, (Cu^{I})
	yellow or orange fluorescence	Au, W(Zn), and also NH_4OH itself
 (VIII)	yellow	Cu^{I}, Au, Ag, Hg^{II}
	orange	Hg^{I}, Cu^{II}, Tl, W, Pt, Pd (Ag)
	orange fluorescence	W, Tl, and also NH_4OH itself
	yellow fluorescence	Au (Zn)

solution. The yellow precipitates or colors formed often have a greenish tint). Vanadium trichloride forms a bluish green solution with rhodanine, the color gradually changes into a yellow-green. Reactions with lead salts in neutral solution, and with salts of bismuth, antimony, manganese, and nickel, and cobalt in ammoniacal solution are only observed after some time – best, after 24 hours. Reactions with stannous chloride and uranyl acetate are only weakly expressed.

TABLE 3

Reactions with Gold Bromide

Reagents	Color of Reagent paper	Colors	50 γ Au	5 γ Au	0.5 γ Au
Rhodanine	Almost colorless	Greyish-yellow	++	++	±
5-Salicylidenerhodanine	Orange	Dark yellow-orange	++	+	±
5-p-Dimethylaminobenzylidenerhodanine	Rose-orange	Rose-violet	+++	+++	±
3-Phenylrhodanine	Colorless	Very light brown	+	+	±
5-Benzylidene-2-thiohydantoin	Yellowish	Yellow	+++	+	−
5-Benzylidene-3-phenyl-2-thiohydantoin	Almost colorless	Yellowish	++	+	−
5-Salicylidene-1-acetyl-2-thiohydantoin	Light yellow	Yellow	+	±	−
5-Salicylidene-3-phenyl-2-thiohydantoin	Light yellow	Yellow	+++	+	−

TABLE 4

Reactions with Silver Nitrate

Reagents	Color	500 γ Ag	50 γ Ag	5 γ Ag	0,5γ Ag
Rhodanine	Brown	+++	+	±	−
5-Salicylidenerhodanine	Dark Orange	+++	++	+	−
5-p-Dimethylaminobenzylidenerhodanine	Violet	+++	++	+	±
3-Phenylrhodanine	Brown	+++	+++	++	±
5-Benzylidene-2-thiohydantoin	Yellow-brown	+++	++	+	−
5-Benzylidene-3-phenyl-2-thiohydantoin	Dirty-violet	+++	++	±	−
5-Salicylidene-1-acetyl-2-thiohydantoin	Brown-yellow	+++	++	+	−
5-Salicylidene-3-phenyl-2-thiohydantoin	Brown-yellow	+++	++	+	−

TABLE 5

Reactions with Mercuric Chloride

Reagents	Color	500 γ Hg	50 γ Hg	5 γ Hg	0.5 γ Hg
Rhodanine	Yellowish	++	−	−	−
5-Salicylidenerhodanine	Orange-yellow	−	−	−	−
5-p-Dimethylaminobenzylidenerhodanine	Rose-violet	+++	+++	++	+
3-Phenylrhodanine	Yellowish	++	++	+	−
5-Benzylidene-2-thiohydantoin	Yellow	+++	++	+	−
5-Benzylidene-3-phenyl-2-thiohydantoin	Yellowish	+	−	−	−
5-Salicylidene-1-acetyl-2-thiohydantoin	Dark yellow	+++	++	±	−
5-Salicylidene-3-phenyl-2-thiohydantoin	Dark yellow	++	+	±	−

5-Salicylidenerhodanine (II). forms a dark orange solution which becomes orange-red on addition of ammonia. The characteristic reactions of this preparation are given in Table 1. There is only a weak reaction between potash alum and ammonium vanadate. A reaction with nickel nitrate is only observed after some time.

Characteristic reactions of 5-p-dimethylaminobenzylidenerhodanine (III) and 3-phenylrhodanine (IV) are given in Table 1. The cherry-red color which is observed on addition of ammonia to a mixture of cuprous chloride and p-dimethylaminobenzylidenerhodanine. very rapidly turns green-yellow. 3-Phenylrhodanine forms with silver in ammoniacal solution a brown colored precipitate. the supernatant liquid is cherry-red. Apart from the tabulated reactions. 3-phenylrhodanine in ammoniacal solution gives rather weakly expressed reactions with the salts of tri- and quadrivalent cerium, barium, trivalent iron, arsenic, antimony, bismuth, tungsten, manganese, cobalt, and thorium.

A comparison of the results for rhodanine and its derivatives shows that all the compounds indicated are characteristic reagents for silver, uni- and divalent mercury, uni- and divalent copper, thallium, palladium, platinum, and gold.

Rhodanine has 3 hydrogens in its molecule, but, in the reactions indicated, simple substitution can only occur as an exception, in view of the fact that rhodanine derivatives in whose molecule the hydrogen atoms indicated, which are in the 3- and also in the 5- positions are replaced by organic radicals, do not lose their specificity. Here, apparently, we have a case of formation of complex compounds with reagent molecule coordinated to cations via the thioketone group $>C=S$, which has, as is known, a large affinity for metals of the hydrogen sulfide group.

Derivatives of 2-Thiohydantoin

The 2-thiohydantoin derivatives indicated in Table 2, have not hitherto been studied as potential reagents for inorganic analysis.

5-Benzylidene-2-thiohydantoin (V) gives in alcoholic solution a pale green-yellow color, which intensifies on addition of ammonia. This preparation gives a cherry-red color with gold bromide, which quickly changes to an orange-brown. Long thread-like crystals with a yellowish color are precipitated after some time when this reagent reacts with zinc sulfate in ammoniacal solution. The precipitate formed with mercuric chloride is in the shape of long needles. There is very little reaction with trivalent cerium salts, and with thallium a reaction is scarcely detectable.

3-Benzylidene-2-thiohydantoin (VI). gives a green-yellow color in alcohol; this color becomes intense yellow on addition of ammonia. This reagent gives a brownish cherry color with gold bromide, which on heating changes to a pale-yellow. The reaction product with cuprous chloride is in the form of thread-like crystals, and with cupric sulfate — the reaction product forms needle-like crystals. There is hardly any reaction with thallium salts.

From what has been said it follows that the introduction of the phenyl group into the 3 position of 2-thiohydantoin has hardly any effect on the specificity of the reagents.

5-Salicylidene-1-acetyl-2-thiohydantoin (VII) gives a yellow color in alcoholic solution, which on addition of ammonia becomes green; an orange fluorescence is given at the same time. Gold bromide gives a yellow-orange fluorescence also, while sodium tungstate gives an orange fluorescence. The fluorescence in ammoniacal solution in the presence of zinc becomes yellower. Extinction of fluorescence in ammoniacal solution is observed with salts of uni- and divalent copper, and also with univalent mercury.

Alcoholic solutions of 5-salicylidene-3-phenyl-2-thiohydantoin (VIII) have a pale yellow color, which becomes paler on addition of hydrochloric acid, but becomes orange on addition of ammonia. Reaction products with cuprous and cupric salts, and also with divalent mercury crystallize as needle-like crystals. Alcoholic solutions of the reagent do not possess any appreciable fluorescence, but on addition of ammonia, acquire an intense orange fluorescence. Fluorescence is also evoked by gold (weak yellow), thallium (weak orange), and tungsten (orange). Extinction of fluorescence in ammoniacal solution, or else a change to a yellow one, is observed with the same ions which gave the same effect with the previous reagent (Cu^{I}, Cu^{II}, Hg^{I}, and Zn).

By comparing the results we got for derivatives of 2-thiohydantoin it is possible to establish that these compounds are characteristic reagents for the same cations, for which rhodanine derivatives are also characteristic, i.e. Ag, Hg^{I}, Hg^{II}, Cu^{I}, Cu^{II}, Tl, Pd, Pt, Au. The only difference is that the reaction with thallium is appreciably weaker. Substitution of hydrogen atoms in the 3- or 1- position by organic radicals has no effect on the specificity of the reaction. It may be noted that the salicylidene derivatives of 2-thiohydantoin can be regarded as characteristic reagents for tungsten and zinc.

Reaction Sensitivity

To check on the sensitivity of the reactions, strips of filter paper were saturated with alcoholic solutions of the reagents. After the strips had been dried, drops of an aqueous solution of silver nitrate containing 500, 50, 0.5, and 0.05 γ Ag^{+} respectively were placed on them. Similar tests were carried out with mercuric chloride and gold bromide,

TABLE 6

The Application of Fluorescence in Reactions with Gold Bromide

Reagents	Fluorescence of the reagent paper	50 γ Au	5 γ Au	0.5 γ Au	0.05 γ Au
Rhodanine	Grey brown	Black-brown	Darker	Darker	—
5-Salicylidenerhodanine	Orange-brown	Dark brown	Brown spots	Darker	—
5-p-Dimethylaminobenzylidenerhodanine	Bright orange	Grey-black	Grey violet	Grey violet	Weak spot
3-Phenylrhodanine	Grey	Grey-brown	Grey-brown spots	Darker	Darker
5-Benzylidene-2-thiohydantoin	Grey-brown	Grey-black	Darker	—	—
5-Benzylidene-3-phenyl-2-thiohydantoin	Grey-green	Grey-green spots	Weak spots	—	—
5-Salicylidene-1-acetyl-2-thiohydantoin	Yellow	Dark-grey	—	—	—
5-Salicylidene-3-phenyl-2-thiohydantoin	Yellow-orange	Grey-black	Dark spots	—	—

TABLE 7

Application of Fluorescence to Reactions with Silver Nitrate

Reagents	500 γ Ag	50 γ Ag	5 γ Ag	0.5 γ Ag	0.05 γ Ag
Rhodanine	Black	Brown	Brown spots	—	—
5-Salicylidenerhodanine	Black	Brown	Brown	Darker	—
5-p-dimethylaminobenzylidenerhodanine	Black	Black brown	Brown spots	Weak spots	—
3-Phenylrhodanine	Black	Brown	Brown spots	Darker	Darker
5-Benzylidene-2-thiohydantoin	Black	Grey-black spots	Grey spots	Grey-violet	—
5-Benzylidene-3-phenyl-2-thiohydantoin	Black	Black spots	Grey spots	—	—
5-Salicylidene-1-acetyl-2-thiohydantoin	Almost black	Brown	Brown spots	—	—
5-Salicylidene-3-phenyl-2-thiohydantoin	Black brown	Red-brown	Brown-violet	Grey-violet	—

with the difference that in the case of gold bromide, the concentration of 500 γ Au was left out. Results are given in Tables 3, 4, and 5. The following notation is used in these tables: + + + indicates a very clearly marked reaction; + + a strongly defined reaction; + weakly defined reaction; ± a reaction can just about be observed.

It follows from the results given in Table 3 for gold bromide, that rhodanine derivatives are more sensitive reagents than 2-thiohydantoin derivatives, thought they have a common functional analytical group. This is undoubtedly connected with the presence of an additional atom of sulfur located in the thiazolidene ring, which, apparently, does not affect the composition of the reaction product, but appreciably enhances reaction sensitivity.

A similar state of affairs is observed in the reactions of test reagents with silver nitrate (Table 4). The picture is different in the case of mercuric chloride (Table 5): this is undoubtedly connected with the very weak auxochromic action of the mercury ion. Rhodanine, its 5-salicylidene derivative, and 5-benzylidene-3-phenylthiohydantoin change their color only when these are fairly large amounts of mercury ions present. This indicates that reactions with mercury should not be carried out on strips of paper, where only a change in color can be observed, but in a test tube, where precipitate formation can be followed.

In the case of mercury compounds, the most intense color is observed with 5-p-dimethylaminobenzylidenerhodanine; this is connected with the presence of an additional strong auxochrome.

We established that direct visual observation of changes in color of paper strips saturated with solutions of reagents, when only vanishingly small amounts of cations are used, suffers from a number of drawbacks, since it depends on illumination, sharpness of vision of the observer, etc. Significantly better results were obtained during fluorescent tests, which we first suggested for detection of a number of metals by means of rhodanine and 2-thiohydantoin derivatives respectively. Although all the reagents indicated do not possess an appreciable fluorescence in solution, the fluorescence becomes apparent on paper strips illuminated with a Bach lamp.

The results given in Table 6, 7, and 8 show that it is possible by means of the fluorescence method to detect, in most cases, considerably smaller amounts of gold, silver, or divalent mercury. In addition, all the changes are far more clear-cut than when the ordinary visual method is used.

Fluorescence tests show that 3-phenylrhodanine is no less sensitive a reagent than p-dimethylaminobenzylidenerhodanine.

TABLE 8

Application of Fluorescence to Reactions with Mercuric Chloride

Reagents	500 γ Hg	50 γ Hg	5 γ Hg	0.5 γ Hg	0.05 γ Hg
Rhodanine	Darker	Weak spots	–	–	–
5-Salicylidenerhodanine	Brown-green	Brown	Brown spots	Brown spots	–
5-p-Dimethylamino-benzylidenerhodanine	Violet	Grey-violet	Dark spots	Weak spots	–
3-Phenylrhodanine	Almost black	Grey-black	Grey spots	Darker	–
5-Benzylidene-2-thiohydantoin	Darker	Darker	Dark spots	–	Darker
5-Benzylidene-3-phenyl-2-thiohydantoin	Darker	Darker	–	–	–
5-Salicylidene-1-acetyl-2-thiohydantoin	Brown-green	Brown	Brown spots	–	–
5-Salicylidene-3-phenyl-2-thiohydantoin	Brown-green	Brown-green	Darker	–	–

SUMMARY

1. Derivatives of rhodanine and 2-thiohydantoin are characteristic reagents for silver, uni- and divalent mercury, uni- and divalent copper, thallium, palladium, platinum, and gold.

2. Reaction specificity is not altered on replacing hydrogen atoms in the 5 and 3 position (in the case of 2-thiohydantoin derivatives, the 1 position also) by organic radicals. This indicates that it is complex formation which occurs and not salt formation.

3. The additional atom of sulfur in rhodanine molecules strongly increases reaction sensitivity with respect to gold and thallium, and also, apparently with respect to silver. Divalent mercury possesses only a very weak auxochromic effect as compared with silver and gold.

4. Salicylidene derivatives of 2-thiohydantoin are characteristic reagents for tungsten and zinc.

5. The clearness of the reaction carried out on paper strips increases considerably on illuminating the strips with fluorescent light; this fact could be used in analytical practice. Strips saturated with solutions of derivatives of rhodanine and 2-thiohydantoin respectively, show a clear-cut fluorescence, which changes sharply during reactions with the cations indicated.

Received January 3, 1955

LITERATURE CITED

[1] J. V. Dubský and V. Černák, Publ. Fac. Sci. Univ. Masaryk, 269, 9, (1939); to C. 1939, II. 176.

[2] J. V. Dubský, V. Šindelář and V. Černák, Mikrochemie, 25, 124 (1938).

[3] F. Feigl, and J. Pollak, Mikrochemie, 4, 185 (1926).

[4] F. Feigl. Z. anal. Chem., 74, 380 (1928).

[5] L. M. Kulberg, A. A. Ponomarev, and N. I. Davidova, J. Anal. Chem., 9, 85 (1954) (T. p. 97)*.

[6] S. A. Voznesensky, "Inner Complex Compounds and their Use in Analytical Chemistry", 1938.

[7] N. M. Turkevich, N. K. Ushenko, and I. M. Kuzmak, Ukrain. Chem. J., 14, 126 (1949).

[8] N. M. Turkevich, O. P. Melnichuk, Ukrain. Chem. J., 16, 459 (1949).

[9] N. M. Turkevich and E. V. Vladzimirskaya J. Gen. Chem., 24, 2010 (1954) (T. p. 1975)*.

[10] N. M. Turkevich and M. P. Makykha, Ukrain. Chem. J., 16, 648 (1949).

[11] B. M. Turkevich and N. M. Turkevich, Ukrain. Chem. J., 16, 558 (1949).

[12] L. Gendelman, Monatsh, 43, 537 (1923).

[13] Ch. Granacher, M. Gero, A. Ofner, A. Klopfenstein, and E. Schlatter, Helv. chim. Acta 6, 458 (1923).

[14] G. Bargellini, Atti reale accad. peloritana, [5], 15, I, 181 (1906).

[15] A. Zipser, Comptes rend., 135, 1118 (1902).

[16] M. Nencki, Ber., 17, 2227 (1884).

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

A CRYOSCOPIC METHOD FOR THE QUANTITATIVE DETERMINATION OF ARENES (AROMATIC HYDROCARBONS) IN PETROLEUM OILS IN CYCLOHEXANE SOLUTION

M. D. Tilicheev, M. S. Borovaya, and V. S. Buk

All-Union Scientific Research Institute for Petroleum Treatment and Production of Artificial Fuel (VNIINP), Moscow

The cryoscopic method which was worked out previously [1], for the quantitative determination of arenes in petroleum lubricating oils, has now been improved and made more accurate in the work described here; in addition, it has been used for the first time for checking on the completeness of separation of arenes from alkanes and cyclanes during chromatographic separation of lubricating oils into arene and saturated fractions respectively, on silica gel. On the basis of the results obtained during tests which are described below, the cryoscopic method which we have developed for the quantitative determination of arenes in lubricating oils can be used as follows.

To 13 ml of cyclohexane with a known crystallization temperature, was added 0.4-0.6 ml, i.e. ca. 1% (mol.) of the test fraction by means of a pipet; the temperature of crystallization of the solution was then determined. This solution was next treated three times, for 20 minute periods, with a mixture of P_2O_5 + H_2SO_4, 1 volume of fresh mixture being taken each time.

After the solution has been treated with the $P_2O_5 + H_2SO_4$, it was given a three-fold treatment with 99% H_2SO_4, each time for 10 minutes and using an equal volume of sulfuric acid; it was finally neutralized, dehydrated over fused calcium chloride, and the crystallization temperature again determined.

Arenes content was determined according to equation (1) derived previously [2]

$$x = \frac{100 \cdot \Delta t_2}{\Delta t_1} \qquad (1)$$

where x – is the aromatic hydrocarbons content in mol. %; Δt_1 – depression of the crystallization temperature of cyclohexane in °C after addition of test mixture; Δt_2 – elevation of crystallization temperature of the solution of test mixture in cyclohexane after removal of arenes by the adopted method.

EXPERIMENTAL

Characteristics of the Original Products and Experimental Procedure

In the present work we used as starting materials components which had been separated chromatographically from oil distillates, and oils obtained from these distillates by sulfuric acid and selective purification. From each distillate or oil, a mixture of alkanes and cyclanes (specific dispersion less than 100) and four fractions of arenes were first extracted in succession. The detailed method of isolating these components, and their properties are described in the article by Borovaya and Krein [2].

Determination of the crystallization temperature of pure cyclohexane and of solutions of test fractions in it, was carried out in a Beckmann molecular weight apparatus. The apparatus consisted of an inner test tube, into which the test product was poured, a glass connecting tube, and a beaker for cooling the mixture.

In order to mix the test solution, the apparatus was provided with an automatic stirrer operated with a small electric motor and an electric magnet.

Temperature of crystallization was measured with a normal thermometer having a scale graduated from –30 to +20° in scale divisions of 0.1°. The temperature was read with a magnifying glass to hundredths of a degree. A mixture of water and ice was used for cooling. The temperature difference between test solution and cooling bath was kept equal to 1-2°.

Chemically pure acid obtained by saturation of 94-95% sulfuric acid with SO_3 was used. H_2SO_4 concentration was determined both by titration and by its crystallization temperature. The phosphorus pentoxide — sulfuric acid mixture was prepared by adding 30 g of P_2O_5 to 100 ml of 99% H_2SO_4 (a 14.0% solution of P_2O_5 in 99% H_2SO_4).

Improvement of the Method Used for Separating Arenes from Cyclohexane — Test Oils Mixtures

In our previous article [1], we suggested, for the removal of arenes, a three fold treatment of a cyclohexane solution with a mixture of H_2SO_4 and P_2O_5, using an equal volume of the mixture each time; this was followed by three-fold treatment with sulfuric acid. The final solution was not neutralized. In order to have a further check on the effect of the number of times the solution was treated with the $H_2SO_4 + P_2O_5$ mixture, and the effect of neutralization of the solution, appropriate experiments were carried out (Table 1).

TABLE 1

Effect of the Number of Times the Cyclohexane Solution of Arenes was Treated with a Mixture of $H_2SO_4 + P_2O_5$, and Subsequent Neutralization of the Solution on the Values Found for the Arenes Content

Experiment	Designation of original Petroleum	Number of arene fractions	Arenes found in mol. %		
			After 2 treatments with the $H_2SO_4 + P_2O_5$ mixture•	After 3 treatments with the $H_2SO_4 + P_2O_5$ mixture•	After neutralization
1	Balakahnsky Oil	IV	—	92.0	95.2
2	Balakahnsky Heavy	III	94.9	97.8	97.8
3	Balakahnsky Heavy	IV	96.3	98.3	98.3
4	Binagadinsky Oil	II	85.0	86.9	87.7
5	Binagadinsky Oil	III	—	92.7	93.4
6	Binagadinsky Oil	IV	93.8	93.8	93.8
7	Lokbatansky Oil	III	—	91.4	94.0

• Followed by three successive treatments with 99.0% H_2SO_4: the mixture was shaken by hand for 10 minutes, each time with an equal volume of fresh acid.

The third extraction with the $H_2SO_4 + P_2O_5$ mixture, in most cases, led to higher values for the arenes found (by 2-3 mol. %). Subsequent neutralization and dehydration of the solution led, in some cases to a further increase in the values for the arenes content (by 1-3%). On the basis of these results therefore, it was decided to extract four times with $H_2SO_4 + P_2O_5$, followed by four washings with 99.0% H_2SO_4, and final neutralization. The cyclohexane solutions were neutralized as follows in order to avoid the formation of stable emulsions. The acid solution was shaken up with finely ground solid sodium hydroxide, after which it was carefully washed with water until it gave a neutral reaction.

When carrying out quantitative determinations of arenes it was essential to make sure that the conditions under which the cyclohexane solutions of test oils were treated, were such that the alkane and cyclanes were untouched, while the arenes were removed completely. We accordingly, made some tests (see Table 2) to find out the effect of treating 1% solutions of alkanes and cyclanes from various petroleum oils in cyclohexane, with the sulfuric acid — phosphorus pentoxide mixture. The results of these tests showed that under the conditions indicated, the crystallization temperature of cyclohexane solutions of the test alkanes and cyclanes, remained unchanged, within the limits of accuracy (± 0.02°).

Only in one case (the third test, Table 2) did the crystallization temperature increase by 0.05°. Even here, the calculated value for the arenes content (−2.7%) did not overstep the limits of accuracy of the cryoscopic method for arenes determination. Thus, the results given in Table 2, allow one to conclude that on treating cyclohexane solutions of oil fractions with a mixture of phosphorus pentoxide and sulfuric acid, the alkanes and cyclanes isolated from the petroleum oils, remain unchanged, if one is to go by the crystallization temperature of the cyclohexane solution. The results given in Table 2, also demonstrate that the alkanes and cyclanes isolated chromatographically from petroleum oils, did not contain observable amounts of arenes.

TABLE 2

Results of Extraction of Cyclohexane Solutions of Alkanes and Cyclanes with a 14% Mixture of Phosphorus Pentoxide and 99.0% Sulfuric Acid

Experiment number	Origin of petroleum alkanes and cyclanes	Crystallization temperature of original cyclohexane in °C	Conditions of treatment with P_2O_5 + H_2SO_4		Conditions for subsequent treatment with sulfuric acid		Crystallization temperature of the solution of alkanes and cyclanes in cyclohexane in °C	
			Number of extractions	Duration of extraction in minutes	Number of extractions	Duration of extraction in minutes	Before treatment	After treatment
1	Balakhansky Oil	6.20	1	30	4	10	2.80	2.80
2	Balakhansky Oil	6.20	1	30	4	10	2.60	2.58
3	Balakhansky Oil	6.19	1	30	2	10	4.33	4.38
4	Balakhansky Heavy	6.30	—	—	3	10	1.86	1.34
5	Balakhansky Heavy	6.30	1	30	3	10	2.46	2.48
6	Balakhansky Heavy	6.30	1	30	3	10	4.20	4.20
7	Binagadinsky Oil	6.36	3	30	4	10	2.80	2.80
8	Bibieibatsky Oil	6.36	1	30	4	10	3.05	3.05
9	Lokbatansky Oil	6.20	2	30	3	10	4.28	4.25
10	Embensky Oil	6.20	2	30	3	10	4.60	4.62
11	BakinskyDiesel fuel	6.20	2	30	3	10	4.54	4.53
12	Bakinsky Deasphaltite	6.20	2	30	2	10	5.10	5.08
13	Bakinsky Compound Oil	6.20	2	30	3	10	4.57	4.60

TABLE 3

Quantitative Determination of Arenes in Individual Fractions of Arenes, Isolated from Oils Chromatographically, by the Cryoscopic Method

Experiment number	Number of the arene fraction	Properties of the arene fractions		Crystallization temperature of cyclohexane in °C	Crystallization temperature of solutions of arene fractions in cyclohexane in °C		Arene content in mol. %
		d_4^{20}	Specific dispersivity $\frac{n_F - n_D}{d_4^{20}} \cdot 10^4$		Before treatment	After treatment	
				Balakhansky Oil			
1	I	0.8948	124.3	6.33	3.50	5.92	85.5
2	II	0.9141	132.6	6.30	3.04	5.78	84.0
3	III	0.9378	143.5	6.33	2.80	6.00	90.7
4	IV	0.9868	174.4	6.35	3.20	6.20	95.2
				Balakhansky Heavy			
5	I	0.9036	127.7	6.31	2.65	5.50	77.9
6	II	0.9431	146.7	6.28	2.86	6.10	94.7
7	III	0.9789	169.9	6.36	3.08	6.29	97.8
8	IV	1.0077	207.9	6.36	2.95	6.30	98.3
				Binagadinsky Oil			
9	I	0.9137	131.9	5.18	2.50	5.18	77.9
10	II	0.9470	152.1	5.51	2.21	5.51	87.7
11	III	0.9710	161.4	6.00	2.27	6.00	93.4
12	IV	0.9988	197.2	6.05	2.82	6.05	93.9
				Bibieibatsky Oil			
13	V	0.8984	124.5	6.35	7.80	5.85	86.0
14	II	0.9138	135.8	5.96	2.48	5.70	92.5
15	III	0.9892	191.4	6.35	3.29	6.12	92.5
				Lokbatansky Oil			
16	I	0.9049	129.5	6.38	2.64	5.85	85.8
17	II	0.9298	143.7	6.36	3.06	5.75	81.5
18	III	—	—	6.39	2.89	6.18	94.0

Note. 1. The values of the density and specific dispersivity of individual fractions are taken from article [3].

2. Conditions of treatment: three successive extractions with an equal volume of a mixture of P_2O_5 + 99% H_2SO_4, each of 30 minutes duration; subsequent four-fold treatment with 99.0% H_2SO_4 (10 minutes each time); neutralization and dehydration of solution.

Checking on the Completness of Separation of Alkanes and Cyclanes from Arenes Achieved by Using a Chromatographic Method

The arene content of arene fractions isolated from various oils by a chromatographic method, was determined by the cryoscipic method described above. (See Table 3). The results obtained showed that the first fractions of arenes contained from 14 to 22 mol. % of unsulfonated impurities. In subsequent fractions, the content of unsulfonated impurities gradually decreased. and in fraction IV. it varied within the limits of 2-7 mol. %.

The results given show that the cryoscopic method developed for the quantitative determination of arenes, can be used for controlling the completness of separation of alkanes and cyclanes from arenes by the chromatographic method.

SUMMARY

1. A cryoscopic method for the quantitative determination of arenes in petroleum oils in cyclohexane solution has been made more accurate.

2. It has been shown that this cryoscopic method can be used for the quantitative determination of arenes, or for the control of the completness of the chromatographic separation of arenes from alkanes and cyclanes.

3. It has been shown that various arene fractions separated chromatographically from petroleum oils, under the conditions we used, contained from 2 to 22 mol. % of unsulfonated impurities.

Received February 7, 1955

LITERATURE CITED

[1] M. D. Tilicheev and M. S. Borovaya. "Transport, Storage, and Use of Petroleum Products" Trans. All-Union Sci. Research Inst. Pet., IV Ed. Moscow-Leningrad. State Fuel Tech. Press 1954, p. 230.

[2] M. D. Tilicheev and N. A. Okinshevich. J. Anal. Chem., 7, 259 (1952) (T. p. 293)*.

[3] M. S. Borovaya and S. E. Krein, "Transport, Storage and Use of Petroleum Products", Trans. All Union Sci. Research Inst. Pet. IV Ed. Moscow-Leningrad. State Fuel Tech. Press, 1954, p. 211.

---

* T. p. = C. B. Translation pagination.

A SEMI MICRO-QUANTITATIVE METHOD FOR THE INDIVIDUAL DETERMINATION OF THE HIGHER NORMAL FATTY ACIDS BY DISTILLATION OF THEIR METHYL ESTERS

L. K. Obukhov

The Institute of Chemical Physics, Acad. Sci. USSR, Moscow

Recently, work on the study of the kinetics and chemistry of oxidation processes in complex chemical systems, in which organic materials participate, have been developed considerably; in particular, oxidation of hydrocarbons to give valuable oxygen-containing products. Accordingly, investigators often come up against the problem of individual determination of the higher normal fatty acids which are formed in many cases during oxidation processes. Naturally, the more widely used methods for determining total acids are not sufficient for obtaining complete information about the chemistry of the formation of these products, and determination of individual acids is necessary.

Of great practical importance is the mechanism of formation of acids during oxidation of hydrocarbons in the liquid phase. It is very important to know in such cases at what point of the hydrocarbon chain the molecule is disrupted during oxidation to give carboxylic acids. Results on the amounts of individual acids permit one to get such information directly.

The basis of the method used during the course of the investigation described here was separation of the acids by distillation of their methyl esters; this method was used for separating the end products of oxidation reactions [1, 2].

Since the amount of acids which are available for analysis is very often small, in developing a method we used comparatively small amounts of the mixed acids. Usually, we took a mixture of acids containing from 0.5-2.5 mg -equivalents of each acid for analysis. Naturally, this fact determined the choice of methods used for methylation and distillation. The mixture of acids was converted into the methyl esters by means of diazomethane, since methylation with diazomethane goes quantitatively, and hardly any side reactions occur. Distillation of the methyl esters was carried out in a carrier which was a carefully purified mixture of hydrocarbons with a continuous distillation range of 60-200°.

Separation of the Mixture of Acids from the Test

The method outlined below for separating the acids from the organic solvent, in the main, resembles the method given by Raine and Garmer [3].

To the original test material, which contained a mixture of other organic materials as well as the mixture of acids, was added in small portions 1-2 ml of an aqueous solution of sodium bicarbonate, after which the neutral organic materials were steam distilled. To the cooled residue, containing the fatty acid salts, which remained in a distillation flask, was added the calculated amount of 1 N H_2SO_4 so as not to add excess acid. The liberated free acids were steam distilled until the distillate was neutral to litmus. The aqueous solution of fatty acids obtained was made alkaline with 0.1 N NaOH, using phenolphthalein test paper (the amount of acids distilled over is checked at the same time), and evaporated carefully on a water bath. It is best to evaporate in a deep porcelain beaker, and carry out evaporation slowly enough to avoid sputtering. Evaporation was carried out to the stage where the residue was just preceptibly damp. The residue was carefully mixed with fine $KHSO_4$ and the liberated fatty acids extracted with several 2-3 ml aliquots of benzene. The acid was completely dissolved after 3-4 extracts. Part of the acid solution was taken for a control titration (the acids were titrated with 0.1 N alcoholic NaOH). The total error after all the various operations involved in isolating the acids did not exceed 1.5-2%. The remainder of the acid solution was used for methylation.

Methylation of the Mixture of Acids with Diazomethane

Gaseous diazomethane was prepared from hydrazine hydrate and chloroform. It should be borne in mind that diazomethane is poisonous, and that any work involving it should be carried out in a well ventilated fume cupboard. The reaction was carried out in a 150 ml glass two-necked flask, provided with a tube for introducing nitrogen, a dropping funnel and a condenser. 3 ml of a solution of solid KOH in hydrazine hydrate (1:5 by weight) was placed in the flask and from the dropping funnel, (dropwise), a 50% alcoholic solution of chloroform was added. A very vigorous reaction takes place at this stage. The yellow diazomethane fumes were taken off with a nitrogen stream and absorbed in pure benzene*.

The stoichiometric equation for methylation of the acids by diazomethane can be written as follows:

$$RCOOH + CH_2N_2 \rightarrow RCOOCH_3 + N_2.$$

The solution of CH_2N_2 in benzene, which is of an intense yellow-green color, was added dropwise to the solution of the acids till a slight turbidity appeared. That the end point is being reached can also be verified by the slowing down of the rate at which the color disappears; at the beginning the yellow color disappears almost instantaneously. If the diazomethane is added too quickly, the mixture becomes very turbid and foams. If, all the same, because sufficient care has not been taken, excess diazomethane has been added, it should be removed—either by heating the solution on a water bath (it should not be heated up to the boiling point of benzene), or by placing a piece of unglazed ceramic in the solution since diazomethane rapidly decomposes on rough surfaces.

It is recommended that a fresh solution of diazomethane in benzene should be prepared every time, since solutions which are allowed to stand deposit flocculent polymerization products of CH_2N_2.

To the solution from which excess diazomethane had been removed, was added 30 ml of carrier solvent, and the mixture subjected to further distillation; the total volume was 45-50 ml.

The author thinks that he should mention the following fact. Attempts to carry out quantitative methylation in the carrier or in other organic solvents (alcohol, carbon tetrachloride) were unsuccessful. Probably, under these conditions, side reactions occur as well as methylation; in particular oxidation by dissolved oxygen, induced by the biradical $CH_2<$, leading to formation of saponifiable products which interfere with the analysis, and simultaneously lead to a breakdown of the fatty acids.

Methylation in benzene proceeds quantitatively and is absolutely pure (i.e. no side reactions).

Fractional Distillation of the Mixture of (Fatty Acid) Methyl Esters

As mentioned already, in view of the small amount of material being handled, fractionation should be carried out with a carrier.

The carrier was prepared as follows: a mixture composed of 2/3 gasoline and 1/3 light kerosene was repeatedly extracted with concentrated sulfuric acid; 15-20 ml lots of sulfuric acid were shaken up with 100-120 ml of the carrier in a separating funnel; the darkened sulfuric acid was removed each time; the operation was repeated until the sulfuric acid, on shaking with the carrier turned only a pale yellow; the carrier was then washed several times with water and boiled with 5% aqueous alkali in a flask fitted with a reflux condenser for 3-5 hours; finally, the carrier was dried over anhydrous Na_2SO_4 and redistilled.

For our tests we used a carrier with a distillation range of 60-200°; before use, the carrier was checked for its content of saponifiables (such as sulfonated compounds); if such compounds were detected, the operation of boiling with alkali was repeated for a longer time, using stronger alkali.

The inner tube of the glass distillation column was 55 cm long and 0.8 cm in diameter. The column was provided with an external regulated heater; heating was controlled exactly, taking into account the difference in temperature at the beginning and end of column operation.

The fractional distillation tube of the column was packed with material prepared according to Levin's method [5]. The packing used was in the form of pieces of nichrome spirals of triangular cross-section, 2.5-3 mm in length,

---

* The mixture heats up appreciably during this reaction. Since diazomethane is explosive, it is advisable not to prepare large amounts of it by this technique. When large amounts are required, it is necessary to carry out the reaction by the usual method, using dilute alcoholic solutions of the reagents [4].

TABLE 1

Temperature Ranges for the Fractional Distillation of Fatty Acid Methyl Esters in a Carrier

Ester	Boiling point in °C in the carrier
$C_4H_9COOCH_3$	95-120
$C_5H_{11}COOCH_3$	125-145
$C_6H_{13}COOCH_3$	150-170
$C_7H_{15}COOCH_3$	170-190
$C_8H_{17}COOCH_3$	195-215

and 1 mm between turns; 1 cm^3 contained up to 200 individual pieces of this packing. The column was equivalent to approximately 50 theoretical plates. When 45-50 ml of liquid was used for each experiment, a distillation took 6-8 hours.

In developing this stage of the analysis for individual pure esters of the acids, we established their temperature ranges for boiling and distillation with the carrier.

As a rule, each ester distilled over completely at a temperature lower than its boiling point over a fairly wide temperature range 20-25°. Probably, this distillation range can be cut down by improving the arbitrary fractionation.

The ester content of each fraction of carrier was determined by saponification with 1 N alcoholic alkali followed by back titration of excess alkali with 0.1 N HCl.

Replicate experiments on the distillation of individual esters with carrier gave coincident results, which are given in Table 1.

TABLE 2

Distillation of Mixtures of the Methyl Esters of Higher Fatty Acids with Carrier

Ester	Temperature of fraction in °C	Amount of ester in mg. equivalents X 10	Total amount of ester		Accuracy of method in %
			Taken in g	Found in g	
	85-90				
	90-95	0			
	95-100	0.54			
$C_4H_9COOCH_2$	100-105	0.58	0.0260	0.0255	99
	105-110	0.50			
	110-115	0.28			
	115-120	0.30			
	120-125	0			
	125-130	0.90			
$C_5H_{11}COOCH_3$	130-135	0.98	0.0455	0.0447	98.5
	135-140	1.00			
	140-145	0.60			
	145-150	0			
	150-155	0.36			
$C_6H_{13}COOCH_3$	155-160	0.84	0.0317	0.0308	97
	160-165	0.62			
	165-170	0.32			
	170-175	0.24			
	175-180	0.48			
$C_7H_{15}COOCH_3$	180-185	0.96	0.0328	0.0326	99.5
	185-190	0.38			
	190-195	0			
	195-200	0.28			
$C_8H_{17}COOCH_3$	200-205	0.52	0.0217	0.0208	96
	205-210	0.22			
	210-215	0.18			
	215-220	0			

It was, moreover, necessary to determine the extent to which the components of a synthetic mixture of the methyl esters of the higher acids are quantitatively separated during distillation with a carrier. Table 2 gives an example of a such a distillation for the five esters corresponding to the acids from valeric to pelargonic acid.

TABLE 3

Results for a Complete Analysis of a Mixture of the following Acids: Valeric, Caproic, Enanthic, and Caprylic

Acid	Amount taken in g	Amount found in g	Accuracy of the method in %
n-valeric $C_5H_{10}O_2$	0.0645	0.0626	96
n-caproic $C_6H_2O_2$	0.0575	0.0540	94.0
n-enanthic $C_7H_{14}O_2$	0.0338	0.0358	104
n-caprylic $C_8H_{16}O_2$	0.0410	0.0414	101

As is evident from Table 2. the esters are separated quite sharply from each other; the boiling ranges established for individual materials are also constant.

Table 3 contains results for a complete analysis of a mixture of acids.

It is therefore clear that the method suggested is very suitable for analyzing mixtures of fatty acids.

Naturally, this method can be used also for isolating individual acids from their mixtures by saponifying the corresponding methyl esters with alkali solution.

The author wishes to thank Professor N. M. Emanuel and D. G. Knorr for their interest in this work.

SUMMARY

A method has been worked out for the individual determination of normal fatty acids in mixtures of these acids. The method consists essentially of preparing the methyl esters of the acids by methylation with diazomethane, followed by fractionation in a column equivalent to 50 theoretical plates.

The method can also be used for preparative separation of individual acids from various industrial fractions by saponification of the corresponding methyl esters with an alkaline solution.

Received May 26, 1955

LITERATURE CITED

[1] Weitkamp, A. W., J. Am. Chem. Soc., 67, 447 (1945).

[2] Schulbuch, H. H., Franzen, V., Ann. Chim. 577, 60 (1952).

[3] Raine, T. Z., Garmer, F. H., Trans. Faraday Soc. 47, 896 (1951).

[4] B. Eistert, An article in the collection "New Methods of Preparative Organic Chemistry" Foreign Lit. Press, Moscow, 1950 p. 91.

[5] A. I. Levin, "Petroleum Economy". No. 10, 40 (1949).

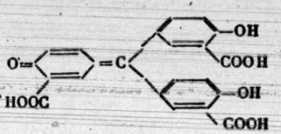
THE ANALYTICAL APPLICATION OF AURINTRICARBOXYLIC ACID

L. A. Molot and L. M. Kulberg•

The N. G. Chernyshevsky Saratov State University

Aluminon – the ammonium salt of aurintricarboxylic acid – has entered analytical practice as one of the best organic reagents for the detection and quantitative determination of traces of aluminum. All the same, from a theoretical point of view, the reagent is far from having been fully studied; in particular, no serious discussion has been published re the structure of aluminum and its lakes. Meanwhile this is of undoubted importance, since only a knowledge of the mechanism of a reaction allows one to choose the correct conditions for carrying out the reaction, and also to evaluate the analytical characteristics, and possibilities of the respective reagents.

Till recently aurintricarboxylic acid has always been classified as a quinoid structure in all papers [1, 2].



The structure of the inner complex salts of aluminon has also been dealt with from this point of view. Such a formula, however, does not correspond to the modern theory of color. A quinoid structure can only be assumed for neutral solutions of aurintricarboxylic acid, that is to say, the least colored.

Diltey and Wizinger [3], as far back as 1926, made the curious observation that intensely colored materials, in the ionoid form, form weakly colored complex compounds with piperidine, at the same time as materials with a quinoid structure, under the same conditions, increase their intensity and the color becomes deeper. These observations were subsequently confirmed by a number of Rumanian investigators [4, 5], and also in the work of Kulberg and Mustafin [6]. Thus, if a pyridine solution of a dye of the triphenylmethane series becomes colorless, or its intensity decreases to an appreciable extent, under the influence of piperidine, this may serve as convincing proof of the absence of a quinoid structure in such a compound.

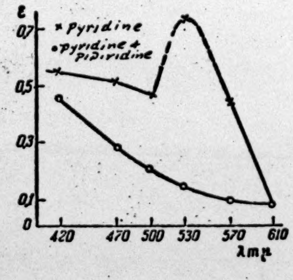


Fig. 1. Absorption curves for a pyridine solution of aluminon, in the absence, and in the presence of piperidine.

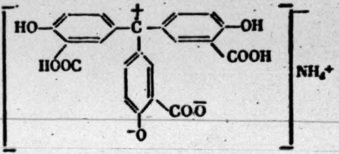
On dissolving a small amount of aluminon (about a few hundredths of a gram) in pyridine, a bright red colored solution is formed; on addition of a few drops of

---

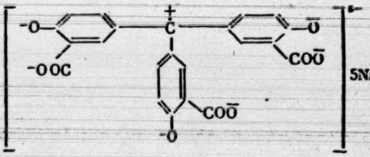
• Deceased.

piperidine, the color changes sharply to yellow. Light absorption curves for a solution of aluminon in pyridine, before and after addition of piperidine respectively, are given in Fig. 1. It is clear from these curves, that not only is the intensity of the yellow color less developed than that of the original red color, but that the shape of the curve also changes considerably.

For weak alkaline solution, on Diltey's theory [7], the following formula would be more correct:



On gradually changing the pH from 7 to 14, as Kuznetsov points out [8], gradual dissociation of the carboxylic and hydroxyl groups occurs in accordance with the values of the dissociation constants of these groups. For strongly alkaline solutions of aluminon, Kuznetsov assumes the following ionoid structure:



The red color of an aluminon solution in a strongly acid media is ascribed by Kuznetsov to a solid phase reaction which occurs under these conditions — insoluble aurintricarboxylic acid is deposited in the form of a fine suspension.

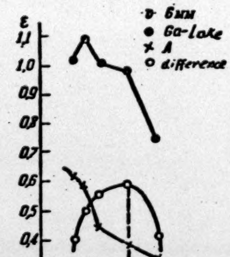
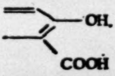


Fig. 2. Determination of the composition of the gallium aluminon lake on the bases of the Ostromyslensky-Dzhub-Babko method.

Babko [9], during a study of the composition of complexes of aluminon with aluminum and iron respectively, established, by a physico-chemical method, that the ratio of aluminon : Al (Fe) = 1 : 1.

We obtained similar results, as can be seen from Fig. 2, during a study of the gallium complex of aluminon. Consequently, of the three cyclo-forming groups which are present in the molecule of aurintricarbosylic acid:



, only one reacts with inorganic ions. The question naturally arises as to the role played by the other groups. By analogy with salicylic acid and its derivatives, we have advanced the view that in aurintricarboxylic acid lakes, there are two internal hydrogen bonds between the carboxy and hydroxyl groups with are ortho with respect to one another [12]. If one makes use of the completely valid analogy between dyes and the reaction products of organic reagents with inorganic ions, which are characterized by an intense color, then it is quite natural to suggest that the presence of an internal hydrogen bond in the molecule of such a compound, should be a factor which

TABLE 1

Comparison of the Sensitivity Limits for Detection of Al^{3+}, Fe^{3+}, and Cr^{3+} by means of Aurincarboxylic Acids

Name of acid aurinmonocarboxylic acid	Limit of identification in 3 ml of solution, in γ		
	Al	Fe	Cr
aurinmonocarboxylic acid	–	3	–
aurindicarboxylic acid	1.2	1	–
aurintricarboxylic acid	0.8	0.5	10

TABLE 2

Molar Extinction Coefficients for the Fe^{3+} lakes of the Aurincarboxylic Acids

Name of acid	E molar
Aurinmonocarboxylic acid	$4.70 \cdot 10^3$
Aurindicarboxylic acid	$6.20 \cdot 10^3$
Aurintricarboxylic acid	$2.20 \cdot 10^4$

enhances the intensity of its color with simultaneous bathochromic shift of the absorption maximum. It is quite possible that the cyclic system formed by closing the hydrogen bond, in playing the part of characteristic auxochromes, will increase the intensity and make the color of the corresponding lakes deeper.

If the assumptions made above are correct, then aurin derivatives partly or completely deprived of hydrogen bonds, should be less valuable as reagents than aurintricarboxylic acid. This problem was resolved experimentally by studying the analytical properties of aurinmono- and aurindicarboxylic acids, and comparing them with those of aurintricarboxylic acid. Qualitative reactions carried out with a number of cations testify to the fact that aurinmonocarboxylic acid is far less reactive, and what is particularly characteristic, it does not react analytically with aluminum and chromium salts; aurindicarboxylic acid, to an even greater extent than aurintricarboxylic acid, gives more or less clear-cut reactions with a large number of ions.

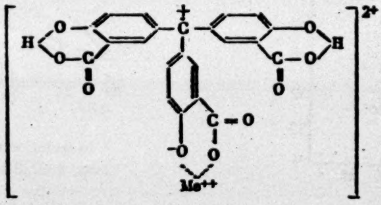
The limits of identification of these three acids for aluminum, iron, and chromium respectively were determined in order to have a quantitative evaluation.

Thus, the reaction sensitivities for all three ions regularly increase with increasing number of carboxylic groups in the reagent molecule.

Even more convincing proof was obtained when we determined the molar light extinction coefficients for the Fe^{3+} lakes of these acids. Table 2 contains the calculated values for molar E.

In his dissertation, Kuznetsov [8], advanced the theory that the lakes formed by aluminon with tri-valent metals possess a definite electrical charge. In order to verify this assumption, a solution of the aluminum lake of aluminon was passed through a column filled with a cation exchange resin. Absorption of the lake by the cation exchange resin, and the absence of any absorption on passing a solution of aluminon itself through the same cation exchange resin gives one more proof of the positive charge of the complex. Another proof of the positive charge on the complex, is the shift of colored lake ions towards the cathode on passing an electric current through a solution of the lake contained in the apparatus used for determining transport numbers.

Taking into account all that has been said above, and the inner molecular dissociation hypothesis of Kuznetsov [10, 11] we should like to put forward the following formula for the salts of aluminon with trivalent metals:



For a final decision of the question, one should also explain whether particles of the lake in solution are in the form of a positively charged sol.

Aluminon reacts with many ions, but chief attention is centered, from an analytical point of view, on its reactions with aluminum, trivalent iron, gallium, and chromium.

Despite the fact that a fairly large amount of work has been devoted to the quantitative determination of aluminum by means of aluminon, hitherto questions of the optimum value of pH for carrying out the reaction, reaction kinetics, the use of ammonium carbonate etc. remain unsolved.

We found out that it is best to carry out aluminum determinations at a pH of 4.4 after 5-10 minutes, always after the same time interval after preparing solutions of the lake. It is advantageous to carry out the reaction in a biphthalate buffer solution which is characterized by a high degree of stability and capacity* [12]. For stabilization of the aluminum lake, which is particularly important during colorimetric determinations, the most suitable stabilizing agent is gum arabic; starch can also be used; the use of gelatine or glycerine for stabilizing the lakes cannot be recommended.

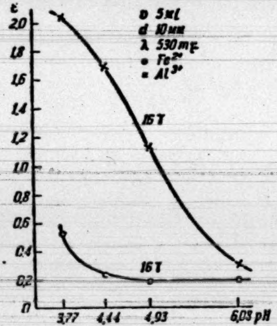


Fig. 3. Change of the optical density of the systems: Al^{3+} - aluminon and Fe^{2+}-aluminon, respectively with pH.

A study of the interaction of iron salts with aluminon is of essential importance, since iron, which reacts with aluminon to form a violet color, masks the reaction with aluminum when these metals are present together.

Reaction sensitivity of iron salts and aluminon is dependent on pH and attains its maximum at a pH of 3.78. Under these conditions it is possible to detect 0.5 γ of iron in 3 ml of solution. In carrying out quantitative reactions, one should use buffer solutions with a pH of 4.0-5.5 or lower, since Fe^{3+} is precipitated at the pH indicated, gum arabic being introduced into the aluminon solution as a stabilizer. At a wave length of λ = 530 mμ, it is possible to determine 5-40 γ of iron in 3 ml of test solution on a Pulfrich photometer.

The fact which Korenman [13], discovered, viz. that there is practically no reaction between Fe^{3+} and aluminon within a certain pH range, is of great importance for developing a method for the determination of aluminum in the presence of iron. From the results given in Fig. 3, it

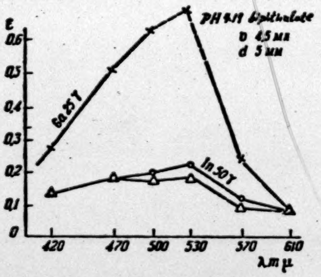


Fig. 4. Absorption curves for solutions of aluminon and its gallium and indium lakes, respectively.

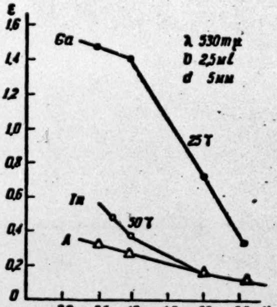


Fig. 5. Change in optical density of solutions of aluminon and its gallium and indium lakes respectively with pH.

---

* Consequently, there is no need to use ammonium carbonate.

follows that at a pH of 4.4. the optical density of an aluminum lake is almost 8 times that of a solution which contains, in the same volume, the reagent and an amount of ferrous iron equal to that of the aluminum. This fact permits one to work out a method for determining aluminum in the presence of small amounts of iron [14]. A cadmium reducer is convenient for reducing Fe^{3+} to Fe^{2+}.

Chromium reacts with aluminon to form a dark red-colored precipitate; this precipitate dissolves in concentrated sulfuric acid to form a red-colored solution. The solution formed, within the concentration range 50-150 γ, obeys Beer's law, so that it is possible to determine chromium quantitatively. Nevertheless, for a variety of technical reasons, this fact has hitherto not gained practical significance; we just give it as one further proof of the possibility of carrying out quantitative determinations of trivalent metals with aluminon.

The clearly defined reactivity of aluminon with gallium, and its much less clearly defined reactivity with indium makes a study of these reactions extremely interesting. It is well known that indium and gallium, which are are complete electronic analogs, gives absolutely identical reactions with most organic reagents hitherto studied. Accordingly, for determination of gallium in the presence of indium it is necessary to separate these elements from one another.

Consideration of the absorption curves for solutions of gallium and indium lakes of aluminon respectively (Fig. 4), leads to the conclusion that it should be possible to find conditions such that gallium could be determined in the presence of indium. In actual fact, at the absorption maximum, at a wave length of $\lambda = 530$ mμ, the absorption curve for the indium lake is scarcely distinguishable from the absorption curve of the reagent itself. A study of the effect of pH on the color intensity of the Ga and In lakes respectively, showed that the best colors develop at a pH of 3.5-4 (Fig. 5). The molar extinction coefficients, calculated according to results obtained at a pH of 4.17, and found to be equal to $E_{mol}\ Ga_{lake} = 1.8 \cdot 10^4$; $E_{mol}\ In_{lake} = 0.4 \cdot 10^4$, indicate that, for the given pH, the color of the Ga lake is 4.5 times as intense as the color of the In lake; while in the pH range 4.4-5.5, the color of the In lake is in general practically negligible, which means that it should be possible to determine gallium in the presence of indium without a preliminary separation. In this connection, therefore, we made a detailed study of the reaction between gallium and aluminon. It was found that at a pH of 4.17 the reaction between gallium and aluminon is comparatively slow. From the curve given in Fig. 6, it follows that despite the continuous increase in extinction over a period of 24 hours, the curve reaches a value after only 5 minutes which does not change very much. Accordingly, the color should not be measured for at least 5 minutes after mixing solutions, and in each case, after a strictly defined time interval.

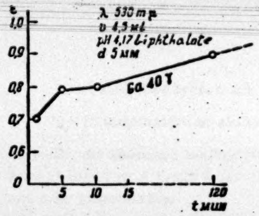


Fig. 6. Change of optical density of a solution of the gallium lake of aluminon with time.

TABLE 3

Determination of Gallium in the Presence of Indium at a pH of 4.17 ($V_{total} = 4.6$ ml)

Ga taken, in γ	In taken, in γ	E at maximum absorption	Ga found, in γ
30	40	0.66	30.2
40	20	0.83	40.5
40	40	0.83	40.5
20	60	0.52	20.4
10	20	0.36	10.2

TABLE 4

Determination of Gallium in the Presence of Zinc ($V_{total} = 6$ ml)

Ga taken, in γ	Zn taken, in mg	$E_{solution}$	Ga found, in γ
20.0	10	0.60	21.5
20.0	15	0.59	21.0
20.0	30	0.58	20.0

The gallium lake of aluminon obeys the Lambert-Beer law (Fig. 7) over a wide concentration range (10-60 γ), so that it is possible to develop a photometric method of determining gallium. Determination is carried out at a pH of 4.17, i.e. under such conditions that traces of indium in solution does not affect analytical accuracy. The results given in Table 3 illustrate what has been said.

The amount of indium in 3.5 ml of test solution should not exceed 60-70 γ, otherwise a positive error, true, only a small one, develops.

At a pH of 5, indium does not react at all with aluminon; accordingly, an even better arrangement is obtained between the amounts of gallium actually taken and that found, when indium is present. A drawback of measurements at this pH, however, is the fact that sensitivity drops off.

Determination of gallium in the presence of zinc is of undoubted practical interest, since these elements accompany each other geochemically.

A study of the interaction between zinc salts and aluminon showed that within the limits of pH 3.5-5.18, there is no appreciable reaction between them. But, at these pH values, the solution becomes turbid and acquires a rose color. This prevents photometric determinations of the solution. On increasing the pH, the interval between the time when the reagents are poured together and the appearance of turbidity increases, while at a pH of 4.6-5.18, the addition of ethyl alcohol to the reaction mixture, increases this time interval. Isopropyl alcohol has an appreciably stronger action. Addition of isopropyl alcohol in an amount approximately 1/3 of the total volume completely prevents the solution from becoming turbid, so that it is possible to carry out photometric measurements.

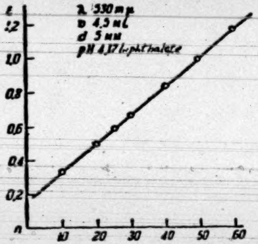


Fig. 7. Calculated curve for gallium determination.

Amounts of zinc up to 25-30 mg, as can be seen from Table 4, do not affect the accuracy of gallium determinations.

SUMMARY

1. A study has been made of the state of aluminon and its lakes in solution.

2. Determination of aluminum by means of aluminon has been made more accurate.

3. An aluminon method has been worked out for the determination of iron and aluminum, when both are present together; a method has also been developed for the determination of gallium in the presence of indium and zinc respectively.

Received March 19, 1954

LITERATURE CITED

[1] L. P. Hammet and C. T. Sottery, J. Am. Chem. Soc., 47, 142 (1925).

[2] F. Feigl, Prog. Chem., 6, 3 (1937).

[3] W. Diltey and R. Wizinger, Ber., 59, 1856 (1926).

[4] E. Cheller, C. A., 32, 5816^5 (1938).

[5] R. Cernatescu, and P. Poni, C. A., 38, 2651^3 (1944).

[6] L. M. Kulberg and I. S. Mustafin, J. Anal. Chem., 7, 84 (1952) (T. p. 97)*.

[7] R. Vitsinger, "Organic Dyes", State Sci. Tech. Press, Leningrad, 1936.

[8] V. I. Kuznetsov, Thesis for Doctorate of Chemical Sciences, Moscow, 1950.

---

* T. p. = C. B. Translation pagination.

[9] A. K. Babko, J. Appl. Chem., 12, 1560 (1939).

[10] V. I. Kuznetsov, J. Gen. Chem., 20, 807 (1950) (T. p. 845).

[11] V. I. Kuznetsov, J. Gen. Chem., 20, 816 (1950) (T. p. 853).

[12] L. A. Molot, Thesis for Candidature of Chemical Sciences, Saratov, 1952.

[13] I. M. Korenman, J. Appl. Chem., 13, 309 (1940).

[14] L. M. Kulberg, N. V. Chugreeva, and L. A. Molot, Cement 6, 21 (1952).

BLANK
PAGE

QUANTITATIVE DETERMINATION OF ETHYLENE GLYCOL AND ITS MONOMETHYL ETHER

I. M. Yurist and Yu. F. Firsova

Ethylene glycol and its monomethyl ether are widely used in various branches of industry, and the question of methods for their quantitative determination is of interest in many industries.

Methods for the quantitative determination of ethylene glycol, described in the literature, are based on its oxidation by various oxidizing agents (solutions of potassium dichromate [1], iodic acid [2, 3], potassium teatraiodomercuroate [4], or the sodium salt of paratoluenesulfonchloramide [5]) with subsequent determination of excess oxidizing agent or oxidation products.

As regards analysis of the monomethyl ether of ethylene glycol, the methods described are oxidation with potassium dichromate [6], or decomposition with hydrogen iodide [7].

The bichromate method which is widely used is not beyond reproach, [1], since some of the condensation products of ethylene glycol which often accompany it (di-, tri-, and polyethylene glycol) are also oxidized to water and carbon dioxide like the monomer; each ethylene glycol residue requires the same number of oxidizing units for its oxidation, as ethylene glycol itself.

In this connection, the "acetin method", which has been introduced into practice for the quantitative determination of glycerol [8], when applied to ethylene glycol, can give more accurate results, since the number of acetylated groups decreases as the molecule becomes more complex. In conjunction with the dichromate method, such a method enables one to estimate the content of hydroxyl derivatives, and also decide on the presence of other oxidizing impurities.

Making use of Petrova's experience [9], who eliminated heating during analysis of primary alcohols by Verley's method [10], we modified the "acetin" method, and showed that acetylation of ethylene glycol and its monomethyl ether with acetic anhydride in the presence of anhydrous sodium acetate proceeds quantitatively even in the cold; thanks to this the acetin method is considerably simplified.

As we showed experimentally (see the tables), such a simplification did not affect the accuracy of determination. The method suggested was checked on concentrated ethylene glycol and its monomethyl ether, which were given a supplementary purification and distilled, and also on their aqueous solutions.

EXPERIMENTAL

Original Products

1. Ethylene glycol, dried over calcined sodium sulfate and redistilled twice

Boiling range 196-197°
d_4^{25} 1.1079

Ethylene glycol content, determined by the dichromate method 98.28%.

2. Ethylene glycol monomethyl ether, treated with a solution of ferrous sulfate, dried over calcined sodium sulfate and twice redistilled:

Boiling range 124-125°
d_4^{20} 0.9638
Monomethyl ether content by Verley's method [10], 100%

3. Acetic anhydride — analytical grade (GOST 5815-52).*

4. Sodium acetate — analytical grade (GOST 199-52), dried gradually in the course of 6 hours, the temperature being gradually raised from 60 to 320° till it is completely dehydrated.

* GOST = All-Union State Standard.

Analytical Procedure

An accurately weighed aliquot of ethylene glycol or its monomethyl ether (ca. 1 g) was introduced into a 700 ml conical flask which contained 5 ml of acetic anhydride; to this mixture was added 3 g of anhydrous sodium acetate, the flask stoppered with a ground glass stopper and the whole left for 4.5-5 hours. At the end of this period 50 ml of distilled water heated to 80°, and free from carbon dioxide, was added; when flask and contents had been cooled completely, the solution was titrated with 0.5 N alkali, using phenolphthalein as indicator, to a pale rose color. Having added 50.0 ml of 1.0 N alkali, the mixture was boiled for 15 minutes, cooled under a stream of cold water and excess alkali titrated with 1.0 N acid to a weak rose color. The content of ethylene glycol or its monomethyl ether was then calculated from the amount of alkali used, by means of the formula:

$$\% \text{ material} = \frac{(a-b) \cdot A \cdot N \cdot 100}{c}$$

where a – is the amount of exactly 1.0 N alkali in mls taken for saponification; b – the amount of exactly 1.0 N acid in mls, used for titrating excess alkali; c – the weight of sample in g; A – the number of grams of material, corresponding to 1 ml of exactly 1.0 N alkali; 0.03103 for ethylene glycol, and 0.07609 for its monomethyl ether; N – normality of the alkali solution.

TABLE 1

Weight of ethylene glycol in g (c)	Weight of ethylene glycol taken calculated on a 100% basis	1.0 N NaOH in ml (a – b)	Ethylene glycol found		deviation in %
			in g	in % of the aliquot	
1.1732	1.1530	37.34	1.1587	98.76	+ 0.48
1.2162	1.1953	38.70	1.2009	98.74	+ 0.46

TABLE 2

Weight of ethylene glycol monomethyl ether in g (c)	1.0 N NaOH in ml (a–b)	Methylene glycol found		Deviation in %
		in g	in %	
0.5254	6.87	0.5227	99.49	–0.51
0.5024	6.62	0.5037	100.26	+ 0.26

TABLE 3

Weight of ethylene glycol in g (c)	Weight of water in g	Weight of ethylene glycol taken, calculated on a 100% basis		1.0 N NaOH in ml (a–b)	Ethylene glycol found		Derivation in %	Relative error in %
		in g	in %		in g	in %		
0.3018	1.4064	0.2966	17.36	9.74	0.3022	17.69	+ 0.33	+ 1.9
0.5074	0.4776	0.4985	50.60	16.25	0.5042	51.18	+ 0.58	+ 1.1

TABLE 4

Weight of methylglycol in g (c)	Weight of water in g	Methylglycol content of mixture in %	1.0 N NaOH in ml (a–b)	Methylglycol found		Deviation in %	Relative error in %
				in g	in %		
0.5278	0.5360	49.61	6.92	0.5265	49.49	–0.12	–0.2

Results obtained for the analysis of ethylene glycol, its monomethyl ether, and their aqueous solutions, by the method described are given in Tables 1, 2, 3, and 4. Accuracy of determination was ± 0.5% absolute.

SUMMARY

It has been shown that the reaction between ethylene glycol and its monomethyl ether, respectively, with acetic anhydride in the presence of anhydrous sodium acetate is quantitative, even without heating; and that it can be used for the determination of these compounds both in the pure state, and also in their aqueous solutions.

Received May 3, 1954

LITERATURE CITED

[1] V. V. Korshak, "Methods of High Molecular Organic Chemistry" Volume 1, Acad. Sci. USSR Press, 1953, p. 445.

[2] L. Malaprade, Comptes rend., 186, 382-4 (1928).

[3] G. Hoepe and W. Treadwell, Helv. chim. Acta., 25, 353 (1942).

[4] P. J. Fleury and Marque, Comptes rend., 188, 1686-8 (1929).

[5] B. N. Afanasef, Factory Labs., 15, 1271 (1949).

[6] H. J. Werner and Mitchell, Ind. Eng. Chem. Anal. ed., 15, 375 (1943).

[7] P. Morgan, Ind. Eng. Chem. Anal. ed., 18, 500 (1946).

[8] K. Bauer, "Analysis of Organic Compounds", Foreign Lit. Press, 1953, p. 85.

[9] L. N. Petrova, J. Anal. Chem., 8, 61, (1953) (T. p. 67)*.

[10] Verley, Bolsing, Ber., 34, 3354 (1901).

[11] K. A. Andrianov and D. A. Kardashev, "Practical Work on Synthetic Resins and Plastics" No. 2, State Chem. Press 1946, p. 140.

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

NEW ACID-BASE INDICATORS FOR LOW pH VALUES

V. I. Kuznetsov and G. N. Kosheleva

All Union Scientific Research Institute of Chemical Reagents, Moscow

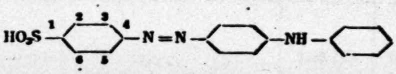
All the range of acid solutions with which one has to deal with in analytical practice, has not, hitherto, been covered by pH indicators suitable for practical application.

Many of the pH indicators described in the literature have some drawbacks. The widely used indicators of the di- and tri-phenylmethane series (crystal violet, methyl violet, malachite green) are quickly decolorized in acid solutions, and give so-called colored solid phase reactions [1], with heavy anions, which distort the observed colors. Other pH indicators have color transitions which are not clearly defined enough, or give unreliable results in the presence of even traces of many elements, as a result of salt errors of a "special type" [2], which are characteristic of these indicators.

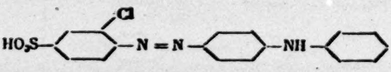
As pointed out in another of our papers [3], azo-indicators of the type of methyl orange and its analogs, are free from these errors. It was shown in the course of the same paper that by introducing substituents into the molecule of the original azo-indicator it is possible to prepare new indicators which change their color in more acid solutions than the original indicator is capable of. Particularly effective in this connection, is the introduction of inert substituents in the ortho position with respect to the azo-group, as a result of the steric hindrance which results and prevents salt formation in the azo group.

Examples of new indicators of methyl orange analogs have been described previously. In the present article we describe the corresponding analogs of the indicator tropeolin-00 (diphenylamine-< 4-azo-4> -benzenesulfonic acid), which were of great interest for strongly acid solutions with very low and negative pH values.

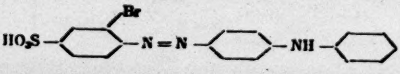
New azo-indicators have been synthesized which differ from the benzenesulfonic acid of 1< 4-azo-4> -diphenylamine



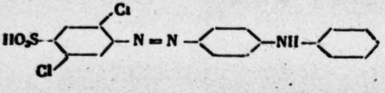
in that Cl and Br atoms are located in positions 3, 5, and 6; they have the following structure:

1.


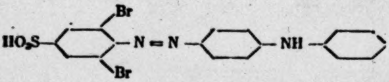
< 4-azo-4> -diphenylamine-3-chloro-1-benzenesulfonic acid

2.


< 4-azo-4-> -diphenylamine-3-bromo-1-benzenesulfonic acid

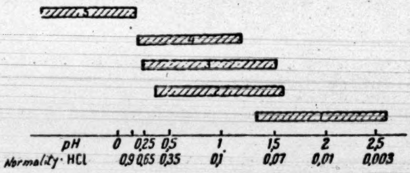
3. 

< 4-azo-4> -diphenylamine-3,6-dichloro-1-benzenesulfonic acid

4. 

< 4-azo-4> -diphenylamine-3,5-dibromo-1-benzenesulfonic acid

The new indicators, like tropeolin-00, give a contrasting color change from yellow in neutral and weakly acid solutions, to violet-red in strong acid solutions. They are completely stable in solution and can easily be prepared.



Transition ranges: 1) Tropeoline-00; 2) Monochloro-substituted; 3) Monobromo substituted; 4) Dichloro substituted; 5) Dibromo substituted.

TABLE 1

pH Values for Half Transition of the New Indicators

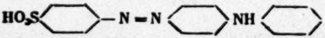
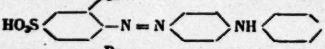
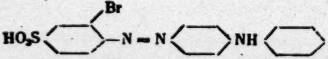
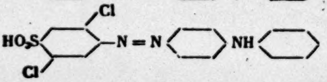
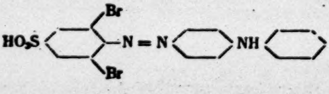
Experimental number	Formula for the indicator	pH for half transition	Transition range
1		1.56 [2]	from pH 1.3 to pH 2.6[2]
2		0.76	from 0.5 N HCl to pH 1.5
3		0.68	from 0.7 N HCl to pH 1.6
4		0.26	from 0.8 N HCl to pH 1.2
5		−0.55	from 4 N HCl to 0.8 N HCl

Table 1 and Fig. 1 give the pH values for half transition of the new indicators; the transition ranges are also given.

It is obvious that the introduction of halogens into the ortho position with respect to the azo group depresses the pH for the half transition of these azo-indicators to a considerable extent; this confirms the conclusions of our previous studies [3].

EXPERIMENTAL

Transition ranges of the indicators were determined by the usual [4]. visual method. The value of the pH at the half way transition was determined by Thiel's method [5]. using a Pulfrich photometer for spectrophotometric measurements. For these determinations 0.001 mol solutions of the indicator in buffer mixtures prepared according to GOST Nos. 4919-49* and in hydrochloric acid solutions of known normality. were used. The pH values of hydrochloric acid solutions were taken from tables [6].

Synthesis of Indicators

1. < 4-Azo-4> diphenylamine 3-chlorobenzene-1-sulfonic acid.

The o-chlorosulfanilic acid necessary for the reaction was prepared by heating o-chloraniline sulfate by Noelting's method [7], and was twice recrystallized from alcohol; its concentration determined by titrating with nitrite was found to be 98%.

0.01 mol (2.1 g) of o-chlorosulfanilic acid was dissolved in 16 ml of water, 2 g of concentrated sulfuric acid was added, and the solution obtained poured onto 15 g of finely crushed ice; diazotization was carried out by adding 0.7 g of sodium nitrite dissolved in 5 ml of water.

The diazonium compound thus prepared was slowly added with cooling and agitation to a solution of 1.8 g diphenylamine (melting point 53-54°) in 6 ml of concentrated sulfuric acid. When addition was complete, the reaction mixture was poured into 100 ml of water, the precipitate formed filtered off, and dissolved by warming in a 10% sodium carbonate solution. Unreacted diphenylamine was removed by filtration. After cooling, the sodium salt of the indicator separated out of solution. This was filtered off and recrystallized a few times from water. An orange colored product was obtained. After drying to constant weight, its nitrogen and chlorine contents respectively, were determined by the Kjeldhal and Stepanov methods [8].

0.2165; 0.1694 g of material: 16.34; 12.26 ml of 0.1 N HCl
Found % N: 10.56; 10.13
$C_{18}H_{13}O_3N_3SClNa$. Calculated % N: 10.25

0.6250; 0.4302 g of material: 12.25; 10.20 ml of 0.1 N $AgNO_3$
Found % Cl: 8.65; 8.40
$C_{18}H_{13}O_3N_3SClNa$. Calculated % Cl: 8.67

2. < 4-Azo-4> -diphenylamine 3-bromobenzene-1-sulfonic acid.

2.5 g (0.001 mol) of o-bromosulfanilic acid (97-5% according to titration with nitrite) was dissolved in 15 ml of water and 2 g of concentrated sulfuric acid added. The solution obtained was poured onto 15 g of finely crushed ice and diazotized by addition of 0.7 g of sodium nitrite dissolved in 5 ml of water.

The diazo compound thus prepared was run into 1.8 g of diphenylamine dissolved in 6 ml of concentrated sulfuric acid. When the solutions had been added together, the reaction mixture was poured into 100 ml of water. Further treatment, purification and analysis of the indicator were carried out as described in the previous case.

0.2296; 0.3032 g of material: 15.30; 20.11 ml of 0.1 N HCl
Found % N: 9.40; 9.28
$C_{18}H_{13}O_3N_3SBrNa$. Calculated % N: 9.25

0.7062; 0.5364 g of material: 15.45; 11.82 ml of 0.1 N $AgNO_3$
Found % Br: 17.50; 17.63
$C_{18}H_{13}O_3N_3SBrNa$. Calculated % Br: 17.62

3. < 4-Azo-4> diphenylamine-3,6-dichlorobenzene-1-sulfonic acid.

0.01 mol (2.4 g) of dichlorosulfanilic acid (98.2%) was diazotized as described above using 0.7 g of nitrite.

---

* GOST = All-Union State Standard.

The diazonium compound was then mixed with 1.8 g of diphenylamine dissolved in 6 ml of concentrated sulfuric acid. The reaction mixture was treated as described above, and the final product purified and analyzed as in the case of < 4-azo-4> diphenylamine-3-chlorobenzene-1-sulfonic acid.

0.1520; 0.1821 g of material: 10.25; 12.33 ml 0.1 N HCl
Found % N: 9.44; 9.48
$C_{18}H_{12}O_3N_3SCl_2Na$. Calculated % N: 9.47

0.3265; 0.2282 g of material: 14.55; 10.05 ml 0.1 N $AgNO_3$
Found % Cl: 15.30; 15.61
$C_{18}H_{12}O_3N_3SCl_2Na$. Calculated % Cl: 16.00

4. < 4-Azo-4> -diphenylamine-3,5-dibromobenzene-1-sulfonic acid.

The dibromosulfanilic acid required for the reaction was prepared by Meinichei's method [9]. Its concentration as determined by titration with nitrite was 97.5%.

0.01 mol (3.8 g) of dibromosulfanilic acid was dissolved in 20 ml of water and 2 g of concentrated sulfuric acid added; the solution was poured onto 15 g of finely ground ice, and diazotised by addition of 0.7 g of sodium nitrite dissolved in 5 ml water.

The diazonium compound was then run into 1.8 g of diphenylamine dissolved in 6.0 ml of concentrated sulfuric acid as indicated above. < 4-Azo-4> -diphenylamine-3,5-dibromobenzene-1-sulfonic acid was purified and analyzed as were the other indicators described above.

0.2326; 0.2005 g of material: 13.54; 11.46 ml 0.1 N HCl
Found % N: 8.14; 8.00
$C_{18}H_{12}O_3N_3SBr_2Na$. Calculated % N: 8.21

Found % Br: 29.61; 29.81
$C_{18}H_{12}O_3N_3SBr_2Na$. Calculated % Br: 30.01

SUMMARY

1. An assumption made earlier, viz. that aminoazo indicators which contain halogens in the ortho position with respect to the azo group change over into the acid form in more acid solutions than the unsubstituted aminoazo indicators has been confirmed.

2. Four chloro- and bromo- substituted tropeoline-00 (< 4-azo-4> -diphenylamine-1-benzenesulfonic acid). These derivatives, like tropeoline-00 form yellow colors in weakly acid solutions and red-violet ones in strongly acid solutions, but they switch over into the acid form at lower pH's than tropeoline-00.

3. The new indicators are suitable for the region extending from 4 N HCl to pH 1.6 which corresponds to 0.03 N HCl.

4. Syntheses of the new indicators are described and the pH values at which they change color are given.

Received February 2, 1955

LITERATURE CITED

[1] V. I. Kuznetsov, Prog. Chem., 18, 75 (1949).

[2] V. I. Kuznetsov, J. Anal. Chem., 5, 365 (1950).

[3] G. N. Kosheleva, Thesis for Candidature of Chem. Sciences, Moscow, 1951, Scientific Archives, Institute of Chemical Reagents.

[4] GOST No. 4919-49 (All-Union State Standard).

[5] Thiel, Fortschr. Chem. Physik, physik. Chem., 18, 1 (1924).

[6] S. D. Beskov, "Determination of Hydrogen Ion Concentration" 1932, p. 78.

[7] Noelting, and Battegey, Ber. 39, 84 (1906).

[8], [9] – No listing in original Russian – Translator.

COLOR REACTIONS FOR FERRICYANIDES WITH DIMETHYLAMINOANTIPYRINE AND TETRAMETHYLDIAMINODIPHENYLMETHANE

A. P. Kreshkov, S. S. Vilborg, K. I. Filippova, and V. A. Drozdov

The D. I. Mendeleev Institute of Chemistry and Technology, Moscow

The methods usually used for detecting ferricyanides include formation of Turnbull's Blue, formation of sparingly soluble salts of silver, copper, and other metals [1], and also methods based on oxidizing properties of ferricyanides: oxidation of benzidene [2], oxidation of dimethyl- and diethylaniline [3], et al. All the reactions mentioned suffer from some defect or other.

Formation of Turnbull's Blue in the presence of ferrocyanides may lead to incorrect conclusions as a result of the ease with which ferrous ions are oxidized to ferric ions, which form Berlin Blue with ferrocyanides, and this latter may then be mistakenly taken for Turnbull's Blue. Preliminary removal of ferrocyanides as Berlin Blue does no good, since ferricyanides are also precipitated [2].

The reaction which is most often used, viz. that based on oxidation of benzidene by ferricyanides, is complicated in the presence of large amounts of ferrocyanides which precipitate benzidene. We have found two new qualitative color reactions for ferricyanides. The first reaction which we would like to propose is based on the formation of a violet colored compound on oxidation of dimethylaminoantipyrine (pyramidone) by ferricyanides. References have been made in the literature to oxidation of pyramidone by nitric acid [4], halogens [5], and the ions of copper [6], and iron [7]. In all these cases a violet color develops. The formula of the oxidation product of pyramidone has not been established.

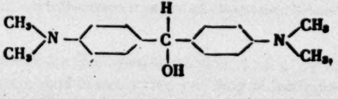
As we showed experimentally, pyramidone is readily oxidized by ferricyanide ions in the presence of zinc ions, which increase the potential of the system $[Fe(CN)_6]^{3-} \rightleftharpoons [Fe(CN)_6]^{4-}$ at the expense of a decrease in the concentration of $[Fe(CN)_6]^{3-}$ ions. E. g. pyramidone is also easily oxidized by ferricyanide ions in a neutral medium in the presence of Cu^{2+}, Mn^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, and Bi^{3+} ions.

A characteristic feature of the oxidation of pyramidone by ferricyanides is the possibility of carrying it out over a wide pH range (from 3 to 9.5).

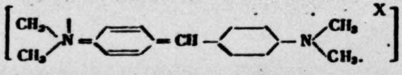
The possibility of carrying out the reaction in an ammoniacal medium makes it specific for ferricyanides, since most of the other oxidizing agents only interact with pyramidone in an acid medium.

The second reaction which we propose for detecting ferricyanides is based on formation of a colored solution when ferricyanides react with tetramethyldiaminodiphenylmethane (Arnold's base) in the presence of zinc salts. Arnold's base, according to published results, on oxidation with PbO_2, MnO_2, Cl_2, and Br_2 in acetic acid solution, gives an intense blue color, which is determined by the formation of a salt which is colorless.

$$(CH_3)_2N \cdot C_6H_4CHOH \cdot C_6H_4N(CH_3)_2.$$



By the action of a moderate amount of acid, this compound undergoes a tautomeric rearrangement and acquires an intense blue color



The color disappears on addition of sodium hydroxide as a result of the formation of the colorless pseudobase.

When acted upon by strong oxidizing agents, e.g. $K_2CrO_7 + H_2SO_4$, Arnold's base may be converted into the quinone and other products. Chlorates, bromates, and iodates do not oxidize Arnold's base.

Arnold's base is used in analytical practice for detecting Au, Ge, Mn, Pb, V, Cl_2, NH_3, and O_3 [8], and for the detection of Mn^{++} ions and periodates by a spot test method [2].

We found that when ferricyanides react with Arnold's base in the presence of zinc salts, oxidation of the base occurs, and a dark or light blue color is observed in solution. In the presence of ferrocyanides, the dye is adsorbed by the precipitate of $K_2Zn_3[Fe(CN)_6]_2$, which is accompanied by coloration of the precipitate a violet-blue. A solution of zinc sulfate is added to complex ferrocyanides formed during the reaction, and to increase the oxidizing potential of the system $[Fe(CN)_6]^{3-} \rightleftharpoons [Fe(CN)_6]^{4-}$.

EXPERIMENTAL

1. Detection of Ferricyanides by means of Dimethylaminoantipyrine

To 1 ml of test solution is added 1 ml of a 2% aqueous solution of pyramidone and 2 drops of a saturated solution of a zinc salt. In the presence of ferricyanides, the solution immediately acquires a violet-blue color, or a precipitate of the same color is formed. The color is not stable, it gradually becomes pale. For a concentration of ferricyanides of 0.5 mg/ml, the color keeps for 10 minutes. In the presence of other oxidizing ions the reaction should be carried out in an ammoniacal medium.

TABLE 1

Determination of Reaction Sensitivity

Concentration of $[Fe(CN)_6]^{3-}$ in mg/ml	Reaction effect
0.50	Blue-violet precipitate
0.25	Blue-violet precipitate
0.05	Violet precipitate
0.025	Violet colored solution
0.010	Rapidly disappearing weak violet color in solution
0.005	No characteristic color

Reaction sensitivity 10 γ. Dilution 1: 200,000.

The spot test technique is as follows: a drop of pyramidone solution, a drop of a saturated solution of a zinc salt, and 1-2 drops of test solution are placed on a porcelain plate. Development of a violet color is observed. It was established experimentally that optimum results are obtained with a 2% aqueous pyramidone solution (melting point of pyramidone 108°) in the presence of 2-3 drops of a saturated solution of zinc acetate. In order to determine the limit of identification a series of experiments were carried out. The results are given in Table 1 and 2.

For these tests 1 ml portions of the ferricyanide solution, 1 ml of pyramidone solution and 2 drops of the saturated zinc acetate solution were used in one series; one drop of ferricyanide solution, and one drop of each of the 2% pyramidone solution, and the saturated zinc acetate solution, in the other.

TABLE 2

Determination of Reaction Sensitivity When a Spot Test Technique is Used

Concentration of $[Fe(CN)_6]^{3-}$ in mg/ml	Reaction effect
0.50	Blue-violet color
0.05	Violet solution
0.025	Weak violet colored solution
0.010	No color

Reaction sensitivity 10 γ. Dilution 1: 120,000

TABLE 3

Determination of Reaction Sensitivity in an Acetic Acid Solution of Arnold's Base

Concentration of $[Fe(CN)_6]^{3-}$ in mg/ml	Reaction effect
0.50	Dark blue precipitate
0.25	Dark blue precipitate
0.025	Dark blue solution
0.010	Light blue solution
0.005	Pale blue solution

Sensitivity 5 γ. Limiting concentration 1:200,000.

2. Detection of Ferricyanides by Means of Tetramethyldiaminodiphenylmethane

To 1 ml of test solution is added a drop of a 2% solution of Arnold's base in acetone, followed by a drop of a 1% solution of zinc sulfate; a blue or light blue color should develop.

The reaction is carried out as follows in acetic acid solution; to 1 ml of test solution is added 1-2 drops of a saturated solution of Arnold's base in 1 N acetic acid followed by a drop of a 1% solution of zinc sulfate. A blue or pale blue color should develop. On carrying out a spot reaction on a porcelain plate, to three drops of test solution is added a drop of a solution of Arnold's base, and a drop of zinc sulfate solution; a pale blue color should develop.

SUMMARY

1. Two new qualitative reactions have been suggested for ferricyanides:

a) a reaction based on formation of a violet colored product on oxidation of dimethylaminoantipyrine by ferricyanides in the presence of zinc ions;

b) a reaction based on formation of a blue colored solution on oxidizing tetramethyldiaminodiphenylmethane with ferricyanides in the presence of zinc.

2. The reactions suggested allow ferricyanides to be detected in the presence of ferrocyanides, chlorates, bromates iodates and some other oxidizing agents.

3. The reactions are fairly sensitive and specific, and do not require complicated apparatus or difficultly available reagents.

Received December 11, 1952

LITERATURE CITED

[1] Treadwell and Hall, "Qualitative Analysis", State Chem. Press, 1946.

[2] Feigl, "Drop Analysis", State Sci. Tech. Press, 1937.

[3] A. P. Kreshkov and S. S. Vilborg, J. Anal. Chem., 3, 250 (1948).

[4] Eschaich, J. pharm. chim., 20, 49 (1919).

[5] A. M. Vasilev, "Trans Commission on Analytical Chemistry", Vol. 1, Acad. Sci. USSR Press, 1947, p. 28.

[6] E. J. King and J. L. Watson, Mikrochemie, 20, 49 (1936).

[7] J. Mellan, Organic Reagents in Inorganic Analysis, Philadelphia, 1941.

[8] L. M. Kulberg, "Synthesis of Organic Reagents", State Chem. Press, 1947.

BLANK
PAGE

AN ANALYTICAL METHOD FOR DIRECT AND ACID AZO DYES

B. M. Krasovitsky, B. I. Ostrovskaya, and D. G. Pereyaslova

The A. M. Gorky Kharkov State University

Various methods have been suggested for the analysis of direct and acid azo dyes; the most important of these are based on reductive splitting of the dye. Thus, reduction of the dye to an amine by stannous chloride [1], or titanium trichloride [2], in acid media is a very widely used method. Nevertheless, reduction by stannous chloride is slow and leads to large deviations in titration results, in duplicate samples of the test solution of the dye. The use of titanium trichloride yields more accurate results, but this reducing agent is not so readily available and is easily oxidized, as a result of which, it is necessary when working with it to take a number of precautions, which complicate the work to a considerable extent. In Shaposhnikov and Geizer's view [3], "determination of titanium numbers demonstrates that it is quite an unsuitable method".

Reduction of dyes by hydrazine in the presence of palladium, like reduction with stannous chloride, is slow and has not been widely used [4]. The use of alkaline solutions of sodium hydrosulfite for the analysis of dyes has also been suggested; these solutions however are readily oxidized and it is not convenient to work with them [5].

Bogoslovsky recently suggested a method based on a new principle for the analysis of direct and acid azo dyes; this consists in adding to a solution of the dye an excess of a standard solution of benzidene hydrochloride to precipitate the benzidene salt of the dye; the precipitate which forms is filtered off, and excess benzidene hydrochloride is determined in the filtrate by titration with alkali, using phenolphthalein as indicator [6]. The drawback of this method is that the filtrate, after removal of the benzidene salt of the dye is usually colored; this either makes titration difficult or impossible when an indicator is used.

In our method we also precipitate the dye from solution as its benzidene salt, but determination of excess benzidene hydrochloride is carried out potentiometrically with sodium nitrite; the end of diazotization is indicated by a potential jump on a platinum electrode.

Our tests confirmed that one molecule of benzidene hydrochloride reacts with two of the sulfonic groups of the dye, as Bogoslovsky noted.

Analytical Procedure. An accurately weighed amount of the dye (0.05-0.1 g) is dissolved in a small amount of distilled water (15-30 ml); the solution is heated to 50° and excess of standard 0.1 N benzidene hydrochloride added (twice the theoretical amount) to precipitate the benzidene salt of the dye. Excess benzidene hydrochloride is filtered from the precipitate into a 100 ml standard flask; the precipitate on the filter is washed with distilled water, the washings being added to the primary filtrate, and the volume made up to 100 ml. A definite volume of this solution is then pipetted out and titrated potentiometrically with 0.01 N sodium nitrite from a micro-buret.

The nitrite was standardized with sulfanilic acid, while that of the benzidene hydrochloride was standardized against sodium nitrite potentiometrically.

Potentiometric titration of benzidene hydrochloride was carried out by means of a micro method, proposed recently by Litvinenko and Grekov [7], whereby it is possible to determine aromatic amines with an accuracy of up to 1%; when analyzing large amounts of dye, we used the same method, but substituted for the micro-buret a normal one. It is necessary to clean the platinum electrode from time to time with chromic acid.

The percentage content of the dye L can be calculated by means of the following equation:

$$L = 100\,\frac{10a - b\,\dfrac{V_{\text{flask}}}{V_{\text{pipet}}}}{c}.$$

where a — is the amount of 0.1 N benzidene hydrochloride in mls taken for precipitation of the dye; b — the amount of 0.01 N nitrite in mls used for titrating excess benzidene hydrochloride; c – the calculated amount of benzidene hydrochloride in mls necessary for precipitating an aliquot of 100% dye.

We analyzed upwards of 30 dyes using this method. The dye to be analyzed was first purified; this consisted in dissolving the dye in water, precipitation from solution by addition of sodium acetate, and finally washing free from acetate by heating with alcohol.

As an example we have given in the table results for the determination of Congo red (weight taken 0.1 g):

TABLE

Experiment number	Dye found in %	Experiment number	Dye found in %
1	74.31	5	74.51
2	73.92	6	74.51
3	74.12	7	75.52
4	75.52	8	74.61

For analysis of other dyes, deviations in results of duplicates did not exceed 3%.

We have already pointed out that the filtrate in which excess benzidene hydrochloride is determined is often colored. This color does not interfere with potentiometric titration, but, one should be able to explain what sort of error this could lead to during analysis, since the color of the filtrate testifies to the fact that either a small amount of the dye has not reacted with benzidene hydrochloride, or that a small amount of the benzidene salt of the dye has dissolved. Regarding the first of these alternatives as the most likely, we compared the colors of filtrates with the colors of specially prepared solutions of the dyes of known concentration on a photoelectric colorimeter. Comparison showed that the amount of dye in the filtrate does not exceed 1% of the weight taken; for most of the dyes we analyzed this amount is smaller.

When working with sample weights of 0.1 g and over it is possible, using the same method for analyzing the dye, to titrate excess benzidene hydrochloride with nitrite from an ordinary buret; in this case however, one should take a larger excess of benzidene hydrochloride for precipitating the dye – 4-5 times the theoretical amount. The use of such an excess permits one to get results of the same accuracy as those obtained when a micro buret is used.

The method suggested can be used for the analysis of all dyes containing the sulfonate groups, and those which form benzidene salts which are insoluble in water.

SUMMARY

A method is proposed for the analysis of direct and acid azo dyes, which permits determination of dye content with an accuracy of up to 3%.

Received June 2, 1954

LITERATURE CITED

[1] R. P. Lastovsky, "Technical Analysis in the Production of Intermediate Products of Dyes", State Chem. Press, 1949, p. 245.

[2] E. Knecht and E. Hilbert, Ber. 36, 1549 (1903).

[3] V. G. Shaposhnikov and G. K. Geizer, Aniline Industry, 10, 445 (1933).

[4] R. Haller and H. Russina, Koll. z. 30, 249 (1922).

[5] Grandmougin and Havas, Chem. z. 36, 1167 (1912).

[6] B. M. Bogoslovsky, Textile Industry, 4, 31 (1953).

[7] L. M. Litvinenko and A. P. Grekov, J. Anal. Chem., 10, 164 (1955) (T. p. 153)*.

---

* T. p. = C. B. Translation pagination.

MUREXIDE, ITS INDICATOR PROPERTIES AND A METHOD FOR ITS PREPARATION

M. M. Sochevanova

Institute of Geological Sciences, Acad. Sci. USSR, Moscow

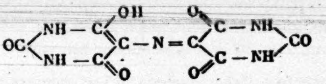
Quantitative determination of calcium in solution can be simplified considerably, if use is made of trilonometric titration.

Trilonometric titration is already being widely used for the determination of total hardness (total calcium and magnesium) in natural [1, 2], and technological waters [3], and also for the analysis of carbonate rocks [4].

Schwarzenbach [5], suggested murexide as an indicator for determining the end point during trilonometric determination of calcium. As a result of the fact that this indicator is not readily available, this volumetric method has not been widely applied in analysis.

Recently, Pribil [6], has described in greater detail the properties of this indicator prepared by the firm of B. Siegfried Zofingen in Switzerland.

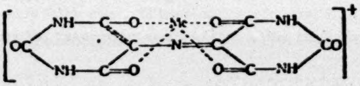
Murexide is the ammonium salt of purpuric acid which has the following structure:



If the anion of this acid is designated R^-, then the formula of murexide will be NH_4R. In acid or neutral media, murexide imparts a red color to the solution, while in alkaline media at a pH > 11, a murexide solution acquires a characteristic lilac (amethyst) color. This change in color can be explained by the fact that in alkaline media, the molecule of murexide dissociates to form the anion of purpuric acid which has a lilac color.

$$NH_4R = R^- + NH_4^+.$$

Murexide forms soluble inner complex compounds with certain divalent metal ions.



In particular, the compound formed with calcium ions has a red color. The formation of this compound can be represented by the equation:

$$\underset{\text{lilac}}{R^-} + Ca^{++} = \underset{\text{red}}{CaR^+}$$

The stability of this complex is appreciably less than that of the complex formed between calcium and Trilon B; accordingly, during volumetric trilonometric determination of calcium, when murexide is the indicator, there is a characteristic color change at the end point from red to lilac.

If Trilon B is designated Na_2H_2Y, the interaction can be expressed by the following equation:

$$\underset{\text{red}}{CaR^+} + Na_2H_2Y \rightleftharpoons Na_2CaY + 2H^+ + \underset{\text{lilac}}{R^-}$$

Trilonometric determination of calcium in the presence of murexide is carried out in an alkaline (NaOH or KOH) medium. Magnesium, under these conditions, in contrast to calcium, does not give a colored compound with murexide. This fact permits direct determination of calcium in the presence of magnesium [5, 7-9].

Murexide can be prepared by the interaction of alloxane or alloxantin with ammonia. In its turn, the synthesis of alloxan or alloxantin, is a complicated and tedious procedure [10, 11].

If one does not set out to prepare a pure compound, but is satisfied with preparing an indicator which is good enough for analytical purposes, the problem can be simplified considerably.

In Cheng and Bray's paper [12], a brief note is made of the possibility of synthesizing murexide by successive treatment on a sand bath of uric acid,first with nitric acid and then with an ammonia solution.

When we followed the instruction of these authors exactly, we did not manage to get a product of satisfactory quality, since, as a result of overheating, most of the product resinified.

During a search for preparing an indicator of good quality, we managed to improve and make the method of preparing it more accurate; the final method developed proved so simple that it can be carried out in any laboratory.

Method for Preparing Murexide

Necessary Reagents: 1) uric acid; 2) nitric acid, concentrated; 3) ammonia, dilute solution (1: 2); 4) potassium sulfate or chloride (as a powder).

Synthesis. 4 g of uric acid is placed in a porcelain basin 12 cm in diameter. Having placed the beaker in a fume cupboard, the uric acid is triturated continuously with 10 ml of strong nitric acid using a glass rod.

The reaction is initially accompanied by copious evolution of nitric oxide fumes, accordingly the indicated amount of nitric acid should be added in 2-3 lots. When the vigorous reaction has ceased, the basin is placed on a boiling water bath and mixing of nitric acid with uric acid continued uninterruptedly, the liquid mass being smeared up to the half way mark on the basin sides.

As heating and evaporation progresses, the mass along the edges of the basin acquires a creamy consistency, while the bulk of the material on the bottom of the basin thicknes to a paste-like consistency. At a certain stage, bubbles start to be evolved again from the mass; at this point one should cease from heating the mass, forwhich purpose it is better therefore to switch off the bath now and again. If the mass should get too hot at this juncture it may foam rapidly, resinify, and attain the wrong consistency.

Evaporation and stirring is continued until gas ceases to be evolved, and the reaction product is converted into a homogeneous yellowish-creamy thick mass. It is characteristic, that if at this juncture there should be ammonia fumes in the air, the material along the basin edges starts to turn a rose color (heating, after addition of nitric acid, takes ca. 30-40 minutes).

The basin is removed from the water bath and allowed to cool slightly. 2 ml of diluted ammonia is added to the still warm mass and the whole rapidly mixed; when this is done the whole mass should acquire a purple-red color. The basin is replaced on the boiling water bath and evaporation and mixing continued until the mass, which has become liquid on addition of ammonia, becomes viscous again; on cooling it congeals to a crumbly mass when picked up on the glass rod. 30-40 g of potassium chloride or sulfate are in the meantime ground up in a mortar to a powder. The purple mass just prepared is removed from the basin walls by means of a spatula and transferred to the mortar containing the powdered potassium salt. The mass of the indicator can be removed readily and completely from the basin, if the basin is warmed during the transfer process on a water bath.

After cooling, the murexide is carefully ground and mixed with the potassium salt until a homogeneous mass is obtained. The product thus prepared is best stored in a dark colored bottle.

100 ml of test solution was taken for trilonometric titration; ca. 50-100 mg of the dry indicator mixture was added. In order to check on the quality of the product obtained by the procedure outlined above, several batches were tested as indicators for the trilonometric titration of solutions of pure salts.

We were mainly interested in determining calcium in the presence of magnesium. For this purpose, known volumes of standard calcium and magnesium solutions respectively, in varying proportions, were diluted with distilled water in conical flasks to give a volume of ca. 100 ml: the solution was made alkaline with 2 ml of 20% KOH (or NaOH), after which the indicator powder was added. The solution, which was colored rose by the indicator, was titrated with Trilon B till the color changed to lilac (amethyst).

When a 0.1 N solution of Trilon B was used, the color change was sharp and could be brought about by one drop. When 0.01 N solutions of Trilon B was used, the color change extended over 2-3 drops.

As an example we have given results for the trilonometric determination of calcium in the presence of magnesium, in the table.

TABLE

Results of Direct Determination of Calcium in the Presence of Magnesium

Taken			Found	
CaO in mg	MgO in mg	MgO/CaO	CaO in mg	Δ
27.65	0.0	0	27.78	+ 0.13
55.30	63.7	1.15	55.30	0.0
41.48	63.7	1.53	41.35	− 0.13
27.65	63.7	2.30	27.65	0.0
13.83	63.7	4.60	13.75	− 0.08
8.30	63.7	7.65	8.15	− 0.15
5.53	63.7	11.50	5.37	− 0.16
2.77	63.7	23.00	2.54	− 0.23
1.38	63.7	46.0	1.34	− 0.04
0.83	63.7	76.5	0.80	− 0.03
0.55	63.7	115.0	0.53	− 0.02
0.28	63.7	230.0	0.27	− 0.01
0.14	63.7	460.0	0.11	− 0.03

As is evident from the table, calcium can be determined with a fair degree of accuracy over a wide concentration range for both calcium and magnesium.

It is of interest to note that the use of murexide opens up the possibility of separated determination of calcium and magnesium in the same aliquot of test solution. In this case, calcium is first titrated with Trilon B using murexide as the indicator; the alkaline solution is then heated to destroy murexide. Excess ammonium chloride is added to the decolorized solution, and after addition of the indicator – Acid Chrome Dark Blue, magnesium is titrated as usual [4].

Strontium and zinc behave similarity to calcium in alkaline solution; they give a color change from geranium-rose to amethyst with murexide.

In accordance with published results [6], murexide can also serve as an indicator for copper and nickel, in addition to the elements listed above; these ions, being themselves colored, give with murexide in ammoniacal media a clear-cut change from a golden yellow to a raspberry on addition of excess Trilon B.

SUMMARY

1. A simple variant has been suggested for the synthesis of murexide.

2. It has been shown that an indicator synthesized by this procedure can be used for trilonometric determination of calcium in the presence of magnesium.

Received August 8, 1954

LITERATURE CITED

[1] W. Biedermann and G. Schwarzenbach, Chimia (Zürich) 2, 56 (1948); and also Helv. Chim. Acta, 31, 678 (1948).

[2] I. Yu. Sokolov, Bulletin of All-Union Inst. Mineral Raw Materials, No. 3 (1953).

[3] G. B. Styunkel, E. M. Yakimets, and D. A. Savinovsky, J. Anal. Chem., 8, 168 (1953) (T. p. 185)* and also Instructions for the Determination of Water Hardness Complexometrically, Ministry of Chem. Ind. Press, Moscow 1952.

[4] M. M. Sochevanova, Bulletin, All-Union Inst. Mineral Raw Materials, No. 4, (1954).

[5] G. Schwarzenbach, W. Biedermann and F. Bangerter, Helv. Chim. Acta, 29, 811 (1946).

[6] R. Pribil, Chem. Listy, 47, 8, 1173 (1953).

[7] E. W. Debney, Nature 169, 4313, 1104 (1952).

[8] K. L. Cheng, T. Kurtz and R. Bray, Anal. Chem., 24, 10, 1640 (1952).

[9] G. Brunisholz, M. Genton and E. Plattner, Helv. Chim. Acta, 36, 782 (1953).

[10] Synthesis of Organic Preparations, Coll. No. 3 Foreign Lit. Press (1952).

[11] L. Vanino, Handb. Prep. Chem., 2, 235 (1929).

[12] K. L. Cheng and R. Bray, Soil Sci., 72, 449 (1951).

---

* T. p. = C. B. Translation pagination.

RAPID METHODS OF MICRO ELEMENTAL ANALYSIS

PART IX. SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN, AND SILICON IN ORGANO-SILICON COMPOUNDS

V. A. Klimova, M. O. Korshun, and E. G. Bereznitskaya

The N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences USSR, Moscow

The chemistry of organo-silicon compounds has now become an important and independent field of organic chemistry, and many organo-silicon compounds have acquired not only theoretical but practical importance. All this naturally has led to an increased demand for quantitative methods of analyzing organo-silicon compounds. Meanwhile, despite the fairly large amount of work devoted to the analysis of these compounds, existing methods do not always satisfy research workers. In the first instance this relates to elemental analysis.

Determination of carbon and hydrogen has usually been carried out by a combustion method according to Liebig-Pregl [1]. Where this has been done, it has been found that organo-silicon compounds during thermal decomposition, form silicon carbide, as a result of which they cannot be oxidized quantitatively. It should be noted that silicon carbide is more readily formed at a higher initial decomposition temperature of a compound [2].

In 1941 Rochow [3], suggested a macro method for the catalytic combustion of highly polymerized organo-silicon compounds in an oxygen stream, for the simultaneous determination of carbon, hydrogen, and silicon; in 1948 [4], he proposed a semi-micro variant of his method. Taking into account the characteristic behavior of organo-silicon compounds during thermal decomposition, Rochow, in his efforts to get over the difficulty of the formation of silicon carbide, carried out his combustion in two stages. He recommended that an aliquot of test sample should first be heated only up to 300-500°; when this is done, slow evaporation of material occurs; subsequently, the vapors, mixed with oxygen, proceed onto a platinum gauze heated to 850°, where they are oxidized to carbon dioxide, water and silicon dioxide. Carbon and hydrogen are determined, as usual, while the silicon dioxide formed is weighed together with the combustion tube in which it is held by means of a plug of glass wool.

Such a method, can, in many instances, give positive results, i.e. it avoids formation of silicon carbide. This method however possesses some disadvantages, since silicon dioxide settling on the platinum, rapidly deactivates the platinum. Moreover, the necessity of weighing all the combustion tube in order to determine the silicon as well, compelled Rochow to decrease the tube dimensions to its limits. The length of the tube used in this method is 18 cm. Combustion of readily volatile compounds in such a short tube is practically impossible, while weighing of an 18 cm tube with a very small amount of silicon dioxide can lead to appreciable errors in silicon determination, even when working with macro weights.

Presumably, the reasons just advanced are responsible for the fact that Rochow's method has not found wide application, particularly for silicon determinations. All the same, we consider his work as a big step forward as compared with methods existing beforehand. Actually, Rochow was one of the first investigators who was not content just to apply mechanically the methods of analyzing organic compounds to organo-silicon compounds, but studied the specific properties of the latter in order to work out his own method. Moreover, Rochow was also absolutely correct in trying to determine the three elements simultaneously on one aliquot; he pointed out in his work that during quantitative combustion of organo-silicon compounds in an oxygen stream, nothing prevents simultaneous determination of silicon along with carbon and hydrogen, since silicon is completely converted into the dioxide.

Apart from Rochow there is no other author who has attempted to develop a method for the simultaneous determination of carbon, hydrogen, and silicon. Since Rochow's method did not satisfy us, now did those of other investigators, we set about developing a reliable method for the simultaneous determination of carbon, hydrogen, and silicon in organo-silicon compounds. We started this work back in 1949 in the Micro Analytical Laboratory of the Institute of Organic Chemistry, and in 1950 had already carried out several analyses[5].

As the basis of our method we used micro and semi-micro methods which we had developed for the rapid analysis of carbon and hydrogen in a rapid stream of oxygen in an unfilled combustion tube, [6]. The basic principle may be outlined as follows: the organic material is subjected to a rapid pyrolytic decomposition with practically no access to oxygen at a temperature of 850-900°. The decomposition products are mixed with a large excess of oxygen, and are oxidized by it at a temperature of 900-950° (the oxygen rate is 35-50 cm^3/minute). Slow evaporation of material is not applicable during analysis by the rapid method. Absorption of interfering elements (N, S, Cl, Br, I) is carried on outside the combustion tube. The apparatus used is simpler than that used for determination of C and H by Pregl's method [7].

The fact that we used an empty tube for combustion and that absorption of interfering elements is carried on outside the tube, allowed us to bring up the problem of developing methods for the simultaneous determination of several elements on one aliquot of test sample [8].

Having decided on this principle we first of all studied the behavior of various types of organo-silicon compounds during their pyrolytic decomposition, and at the same time tried to clarify why the Rochow method discussed above, involving a two stage combustion, helps to avoid formation of silicon carbide.

As we showed experimentally [9], not all classes of organo-silicon compounds form silicon carbide under the conditions normally used for the rapid combustion method. Thus, compounds with a naphthyl radical and containing little hydrogen, burn, as a rule, without any carbide formation, while in the case of aliphatic compounds, the carbide is very readily formed. Further, if before combustion, some water is added to compounds with naphthyl radicals, silicon carbide is formed when such a moist compound is burnt. E.g. during the combustion of methylnapthylsilanediole the following results were obtained:

Material	Calculated	Found	
		during ordinary combustion	during combustion in the presence of water
$CH_3C_{10}H_7Si(OH)_2$	C % — 64.90	65.19	64.56
	Si % — 13.70	13.78	14.50

During combustion with water in a beaker, there remained a black incombustible residue.

In the light of these results one can suggest that during combustion by the Rochow method, the following oxidation process occurs. Heating the test sample to 300-500° leads not only to its evaporation, but to partial decomposition also; when this occurs in the first instance oxidation of a large part of the hydrogen of the test material takes place, and evaporation of the water formed from the comustion zone. This process can be followed by the formation of a drop of water at the end of the combustion tube which appears there right at the beginning of combustion.

Removal of water from the combustion zone apparently favors further quantitative oxidation. It can be concluded from this that the presence of a large amount of water in the decomposition zone favors formation of silicon carbide.

Since, during rapid combustion, pyrolysis of test material is carried out in a quartz beaker, then during analysis of organo-silicon compounds which do not form carbide, there is a possibility of determining not only carbon and hydrogen, but silicon as well, by weighing the beaker together with the silicon dioxide formed in it. It is accordingly possible to determine simultaneously C, H, and silicon on one aliquot of 3-15 mg. Naturally, in this instance, it is essential that all the silicon dioxide should remain in the beaker. It turned out that when pyrolysis was carried out rapidly and completely, we managed to carry out determinations on compounds with naphthyl and alkoxy radicals.

On the other hand, tetralkylsilanes require a special combustion technique, in which pyrolysis is carried out at a lower temperature; consequently pyrolysis is slower and not complete. We did not succeed in carrying out decomposition of these compounds by another technique either, without formation of silicon carbide. This method was not fully satisfactory since part of the silicon dioxide formed was carried beyond the beaker and errors in its determination amounted to 0.8%.

In order to avoid formation of silicon carbide during rapid and complete pyrolysis, and to get good results for silicon, we switched over to work in the presence of a catalyst [10]. As catalyst we used specially prepared chromium oxide on asbestos, which was placed directly in the vessel used for decomposition.

Chromic oxide as a catalyst for surface burning was used by Fedoseev and Pavlenko [11]. form acro-elemental analysis, and proved in our case a sufficiently active oxidizing agent, whereby it was possible to avoid formation of silicon carbide during thermal decomposition of organo-silicon compounds. Thanks to its fibrillar structure, asbestos serves as a good filter for trapping finely dispersed silicon dioxide. By decomposing the material by the rapid method in the vessel used for decomposition, which is filled with chromic oxide placed on asbestos, we successfully carried out simultaneous determination of C, H, and Si in many organo-silicon compounds of the most diverse structure. The presence of oxygen and nitrogen in the material did not interfere with determination.

Simultaneously and independently in 1951-1952. Kreshkov and Guretsky [12]. developed a method for the determination of C and H in organo-silicon compounds. In contrast to us, they did not attempt to determine silicon at the same time as C and H. These authors, according to them, also started off on the basis of the rapid method we developed for the determination of C and H in organic compounds; in their case however they departed from the basic principle of the rapid method, presumably, because they had not grasped the principle. Actually, Kreshkov and Guretsky carried out a slow evaporation of material in the heated zone. In our description of the rapid method however, we emphasized several times, that the method of decomposing the material plays a decisive role in this method [13]. In order that oxidation by a rapid stream of oxygen should proceed quantitatively, it is absolutely essential that the material be not evaporated, rather it should be given a preliminary pyrolysis, so that it is not the vapors which are subjected to oxidation, but the products of pyrolytic decomposition. Insofar as Kreshkov and Guretsky recommend that evaporation be carried out slowly, their use of a beaker instead of a boat is in this instance incomprehensible, since the latter is far more suitable for evaporation, as is also their purpose in adding cupric oxide, which, at low temperatures, cannot favor oxidation of the compound*. By using the method they described, Kreshkov and Guretsky, as a matter of fact returned to Rochow's method, merely complicating affairs by adding cupric oxide and making the method less valuable by not determining the silicon. A rapid oxygen stream and the absence of a platinum contact, naturally, do not essentially change the method, but only compel the authors to lengthen the combustion zone and to increase the temperature to 1050°**.

Accordingly, to date, four methods have been suggested for determining the elements in organo-silicon compounds by combustion of the latter in an oxygen stream. In Table 1 the basic features of these methods are indicated. Hitherto no reliable method for the simultaneous determination of carbon, hydrogen, and silicon has been available. The method which we have developed permits this to be done rapidly and easily. Below we give a description of the analytical method used and the results we obtain for the determination of C, H, and Si.

Analytical Method

Preparation of Catalyst. 1-2 g of ammonium chromate or dichromate is heated with a weak flame in a crucible with a capacity of ca. 50 ml. The powdered chromic oxide thus prepared is mixed with fibrillar asbestos preliminarily calcined at 1200° for 4-6 hours [15]. The catalyst is sieved through a sieve with 2-3 mm openings so as to free it from asbestos dust and excess chromic oxide. The catalyst prepared in this way has a green color and a fibrillar structure; to remove moisture which may have been absorbed during sieving, it is heated in an oxygen stream in a combustion tube at 900-950°. To the end of the combustion tube a Pregl's apparatus filled with anhydrone, which is weighed every hour, is connected. When the weight is constant, between the limits of 100-300 μg. drying can be stopped. This process normally takes 3-4 hours.

Apparatus. The apparatus normally used for the rapid method of determining C and H is employed (Fig. 1).

Analytical Procedure. Combustion is carried out according to the rapid method for determining C and H with an oxygen rate of 35-50 ml/minute; the temperature of the empty combustion tube is 900-950°.

---

* According to our observations [10], cupric oxide, and also platinum do not prevent formation of silicon carbide even at high temperatures.

** We wish to make a point of this in order to emphasize the distorted impression of our method given in the book by Kreshkov and co-authors [14].

TABLE 1

Methods	According to Pregl or Friedrich	According to Rochow	According to Kreshkov and Guretsky	According to our method
Elements determined	C and H	C, H and Si	C and H	C, H and Si
Oxygen rate in ml/minute	4-5	4-5	30-50	35-50
Filling used for combustion tube	Universal or platinum contacts	Platinum contacts	Quartz	None
Length of oxidizing zone in mm	200	100-120	335	110
Temperature conditions:				
a) temperature of evaporation or decomposition of material	750°	300-500°	300-500°*	850-900°
b) temperature of oxidizing zone of the combustion tube	750°	850°	900-1050°	900-950°
Combustion time in minutes	35-40	35-40	35-40**	10-20
Oxidizine agent mixed with test material	$K_2Cr_2O_7$	None	CuO	Cr_2O_3 + asbestos
Methods of decomposition	Slow evaporation (boat)	Slow evaporation (boat)	Slow evaporation (beaker)	Rapid pyrolysis (beaker)

---

* Presumably, 300-500°, since the authors use a small flame for evaporation; they do not say what the exact temperature was.

** Presumably, 35-40 minutes, since the whole analysis takes 1.5 hours.

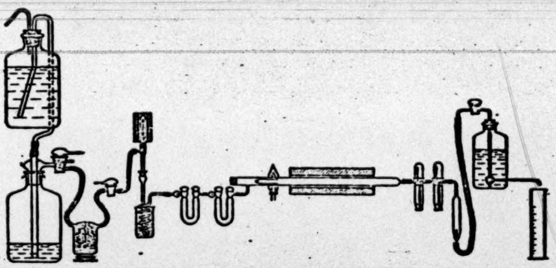


Fig. 1. Set up for simultaneous determination of carbon, hydrogen, and silicon.

In the case of solid compounds or non-volatile liquids, 3-12 mg of sample in a quartz beaker 60-80 mm long and 7-8 mm diameter is used. Aliquots of volatile liquids are taken in a capillary. The sample should be introduced carefully onto the bottom of the beaker; when material gets on the walls, loss of silicon during combustion is possible. When the sample has been taken and the weight of beaker, and beaker + sample have been registered, the catalyst is added, the beaker being filled to roughly 3/4 of its length (Fig. 2), and the whole reweighed. The catalyst should lie in a loose layer; normally, ca. 100-200 mg is required. If the sample is taken in a capillary, then the capillary should be placed in the beaker containing the catalyst and the capillary broken inside it. The capillary should be pushed right into the beaker, otherwise its glass may stick to the tube.

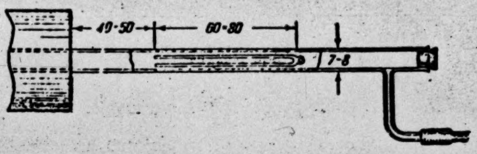


Fig. 2. Arrangement of beaker + sample + catalyst in the combustion tube.

The beaker is placed in the combustion tube at a distance of 4-5 cm from the oven. Before the beaker has been placed in position in the combustion tube, the apparatus for absorption of H_2O and CO_2 is connected; if the compound contains nitrogen as well, then an apparatus for absorbing oxides of nitrogen [16]. is placed between them; combustion is started using the roaring flame of the burner, moving it gradually from the open end of the beaker to the closed end, i.e. against the oxygen stream. Combustion is carried out somewhat slower than is done for rapid determination of C and H in organic compounds, so as not to get a sudden flare-up of material which might expell the catalyst from the beaker. After combustion, one should watch for water vapor settling at the end of the combustion tube. It takes 10 to 20 minutes to complete combustion. A control determination should be carried out, e.g. combustion of any organic material, as saccharose, under the same conditions, so that if necessary, one can introduce the respective corrections for C, H, and Si.

TABLE 2

Compounds Containing C, H, and Si

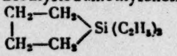
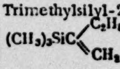
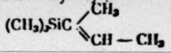
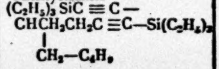
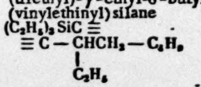
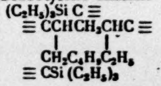
Experiment number	Material	% C			% H			% Si		
		Found	Calculated	Difference	Found	Calculated	Difference	Found	Calculated	Difference
1a	Dibutyldiallylsilane	75,01	74,92	+0,09	12,62	12,58	+0,04	12,37	12,50	—0,13
	$(C_4H_9)_2Si(CH_2CH=CH_2)_2$	74,98		+0,06	12,66		+0,08	12,70		+0,20
2a	Methylnaphthyldiallylsilane	80,83	80,89	—0,06	8,02	7,99	+0,03	11,25	11,12	+0,13
	$C_{10}H_7CH_3Si(CH_2CH=CH_2)_2$	80,84		—0,05	8,11		+0,12	11,04		—0,08
3a	Methylphenyldiallylsilane	77,27	77,17	+0,10	8,82	8,96	—0,14	13,90	13,87	+0,03
	$C_6H_5CH_3Si(CH_2CH=CH_2)_2$	77,11		—0,06	8,94		—0,12	13,60		—0,27
4a	Tetravinylsilane	70,49	70,52	—0,03	8,91	8,88	+0,03	20,82	20,60	+0,22
	$(CH_2=CH)_4Si$	70,71		+0,19	8,92		+0,04	20,71		+0,11
5a	Symmetrical bis-trimethylsilylethylene	56,06	55,75	+0,31	11,82	11,69	+0,13	32,59	32,56	+0,03
	$(CH_3)_3SiCH=CHSi(CH_3)_3$	55,99		+0,27	11,69		0,00	32,35		-0,21
6b	Diethyltetramethylenesilane	67,77	67,53	+0,24	12,85	12,75	+0.10	19,70	19,72	—0,02
		67,70		+0,17	12,60		—0,15	19,55		—0,17
7c	Butyldiallylsilane	71,55	71,35	+0,20	11,95	11,97	—0,02	16,25	16,68	—0,43
	$C_4H_9SiH(CH_2CH=CH_2)_2$	71,36		+0,01	11,90		—0,07	16,60		—0,08
8c	Trimethylsilyl-1-butene-1	65,64	65,54	+0,10	12,76	12,57	+0,19	22,14	21,88	+0,26
	$(CH_3)_3SiCH=CH—CH_2CH_3$	65,67		+0,13	12,41		—0,16	22,01		+0,13
9c	Trimethylsilyl-2-butene-1	65,67	65,54	+0,13	12,41	12,57	—0,16	21,97	21,88	+0,09
	 $(CH_3)_3SiC(C_2H_5)=CH_2$	65,73		+0,19	12,45		—0,12	22,00		+0,12

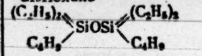
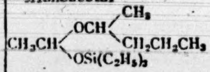
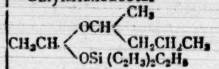
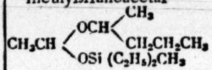
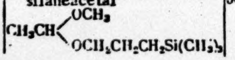
TABLE 2 (continued)

Experiment number	Material	% C			% H			% Si		
		Found	Calculated	Difference	Found	Calculated	Difference	Found	Calculated	Difference
10c	Trimethylsilyl-2-butene-2  $(CH_3)_3SiC(CH_3)=CH-CH_3$	65,41 65,51	65,54	—0.13 —0,03	12,47 12,43	12,57	—0,10 —0,14	21,76 22,00	21,88	—0,12 +0,12
11d	Tripropylvinylethinylsilane $(C_3H_7)_3SiC\equiv CCH=CH_2$	74.81	74,92	—0,12	11,70	11,61	+0,09	12,85	12,46	—0,61
12d	Dimethyldivinylethinylsilane $(CH_3)_2Si(C\equiv C—CH—CH_2)_2$	74.58	74,96	—0,38	8,08	7,96	+0,12	17,12	17,50	—0,38
13d	Dipropyldivinylethinylsilane $(C_3H_7)_2Si(C\equiv CCH=CH_2)_2$	77,70	77,67	+0,03	9,11	9,24	—0,13	13,28	12,94	+0,32
14d	Dimethylphenylvinylethinylsilane $(CH_3)_2C_6H_5SiC\equiv$ $\equiv C-CH=CH_2$	77,50	77,35	+0,15	7,38	7,52	—0,14	14,80	15,08	—0,28
15d	Dimethyltolylvinylethinylsilane $(CH_3)_2(CH_3C_6H_4)SiC\equiv$ $\equiv CCH=CH_2$	77,89	77,91	—0,02	7.93	7,99	—0,06	14,20	14,00	+0,20
16d	Triethyl-1-octinylsilane $(C_2H_5)_3SiC\equiv C-CH_2CH_2C_4H_9$	74,98	74,92	+0,06	12,62	12,57	+0,05	12,37	12,51	—0,14
17d	Triethyl-(γ-triethylsilylbutinyl-δ-butyl) vinylethinylsilane  $(C_2H_5)_3SiC\equiv C-CH(CH_2-C_4H_9)CH_2CH_2C\equiv C—Si(C_2H_5)_3$	73,77	73,77	0,00	11,78	11,87	—0,09	14,43	14,36	+0,07
18d	Triethylisododecynesilane (triethyl)-γ-ethyl-δ-butyl-(vinylethinyl) silane  $(C_2H_5)_3SiC\equiv$ $\equiv C-CH(C_2H_5)CH_2-C_4H_9$	76,01	76,11	—0,10	12,62	12,77	—0,15	11,27	11,11	+0,16
19d	Diacetylene disilane  $(C_2H_5)_3SiC\equiv$ $\equiv CCH(CH_2C_4H_9)CH_2CH(C_2H_5)C\equiv$ $\equiv CSi(C_2H_5)_3$	74,17	74,50	—0,33	11,96	12,03	—0,07	13,69	13,47	+0,22

Notes. a) These compounds were kindly given to us by V. F. Mironov from the Laboratory for the Chemistry of Hydrocarbons; b) these compounds were kindly given to us by N. A. Momma from the Laboratory for Catalytic Synthesis; c) these compounds were kindly presented by G. I. Nikishin from the Laboratory for the Chemistry of Hydrocarbons; d) See Bull. Acad. Sci. USSR, Gen. Chem. Sci. 1954, No. 4. 723. A. D. Petrov, S. I. Sadykhadze and Yu. P. Egorov (C. B. Translation pagination 621).

TABLE 3

Compounds Containing G. H. Si. and O

Experiment number	Material	% C			% H			% Si		
		Found	Calculated	Difference	Found	Calculated	Difference	Found	Calculated	Difference
1b	1,2-Dibutyltetraethyldisiloxane 	63,81 63,73	63,51	+0,30 +0,22	12,68 12,61	12,67	+0,01 −0,06	18,73 18,59	18,55	+0,18 +0,04
2c	Hexamethyldisiloxane $(CH_3)_3SiOSi(CH_3)_3$	44,37 44,14	44,39	−0,02 −0,25	11,12 11,22	11,18	−0,06 +0,04	34,74 34,72	34,57	+0,17 +0,15
3e	Trimethyl-α-dyroxyethylsilane $(CH_3)_3SiCH(OH)CH_3$	50,63 50,50	50,80	−0,17 −0,30	11,79 12,01	11,85	−0,06 +0,16	23,54 23,49	23,79	−0,25 −0,30
4f	Secondary-amyltriethylsilaneacetal 	63,67 63,67	63,36	+0,31 +0,31	12,20 12,17	12,27	−0,07 −0,10	10,96 11,26	11,38	−0,42 −0,12
5f	Secondary-amyldimethylethylsilaneacetal 	60,57 60,48	60,49	+0,08 −0,01	12,10 12,08	12,00	+0,10 +0,08	13,16 12,82	12,85	+0,31 −0,03
6f	Secondary-amyldiethylmethylsilaneacetal 	62,06 62,21	62,01	+0,05 +0,20	12,03 12,11	12,14	−0,11 −0,03	12,04 12,06	12,07	−0,03 −0,01
7f	Methylpropyltrimethylsilaneacetal 	56,53 56,50	56,73	−0,20 −0,23	11,32 11,50	11,65	−0,33 −0,15	14.74 14,45	14,74	0,00 −0,29

Notes. b) See notes to Table 2; c) see notes to Table 2; e) these compounds were kindly presented to us by V. A. Ponomarenko from the Laboratory for the Chemistry of Hydrocarbons; f) these compounds were kindly given to us by I. A. Shikhiev from the Laboratory for Vinyl Compounds.

When combustion is complete, the apparatus for absorption of water and carbon dioxide, and also the beaker with the catalyst still remaining in it + silicon dioxide, are weighed together.

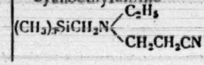
Calculations. Calculations are carried out as follows:

$$\% \mathrm{C} = \frac{K_{CO_2} \cdot a \cdot 100}{N}; \quad \% \mathrm{H} = \frac{K_{H_2O} \cdot b \cdot 100}{N}; \quad \% \mathrm{Si} = \frac{K_{SiO_2} \cdot m \cdot 100}{N},$$

where $K_{CO_2} = 0.2729$; $K_{H_2O} = 0.1119$; $K_{SiO_2} = 0.4672$; a) increase in weight of CO_2 in mg; b) increase in H_2O in mg; m) increase in weight of SiO_2 in mg; N) sample weight in mg.

TABLE 4

Organo-silicon Compounds Containing Nitrogen

Experiment number	Material	% C			% H			% Si		
		Found	Calculated	Difference	Found	Calculated	Difference	Found	Calculated	Difference
1	β-(Dimethylethylsilylmethoxy) propionitrile $(CH_3)_2C_2H_5SiCH_2OCH_2CH_2CN$	56,13 56,12	56,10	+0,03 +0,02	10,00 10,10	10,00	0.00 +0,10	16,29 16,26	16,38	—0,09 —0,12
2	β-(Trimethylsilylpropoxy) propionitrile $(CH_3)_3SiCH_2CH_2OCH_2CH_2CN$	58,41 58,18	58,33	+0,08 —0,15	10,54 10,53	10,44	+0,10 +0,09	14,71 15,03	15,14	—0,43 —0,01
3	Methyldimethoxysilylmethylethylamine $CH_3Si(OCH_3)_2CH_2NHC_2H_5$	44,16 44,37	44,18	—0,02 +0,19	10,31 10,41	10,49	+0,18 —0,08	17,11 16,86	17,19	—0,08 —0,33
4	Trimethylsilylmethylethylamine $(CH_3)_3SiCH_2NHC_2H_5$	54,79 54,91	54,88	—0,09 +0,03	13,16 13,07	13,07	+0,09 0,00	21,31 21,52	21,38	—0,07 +0,14
5	β-(Trimethylsilylmethoxy) propionitrile $(CH_3)_3SiCH_2OCH_2CH_2CN$	53,61 53,46	53,46	+0,15 0,00	9,77 9,61	9,61	+0,16 0,00	17,43 17,84	17,84	—0,41 0,00
6	Siliconeopentylethyl-β-cyanoethylamine  $(CH_3)_3SiCH_2N\left\langle\begin{matrix}C_2H_5\\CH_2CH_2CN\end{matrix}\right.$	58,66 58,66	58,62	+0,04 +0,04	10,95 11,04	10,95	0,00 +0,09	15,45 15,42	15,24	+0,21 +0,18

Notes. The compounds included in this table were kindly given to us by V. F. Mironov from the Laboratory for the Chemistry of Hydrocarbons.

Analytical Results. Using this method we carried out analysis of C, H, and Si in more than 100 organosilicon compounds of the most diverse structure (Tables 2, 3, and 4).

SUMMARY

A method has been developed for the direct and simultaneous determination of C, H, and Si in organisilicon compounds of any structure. Experimental error does not exceed ± 0.3% for C and H, and ± 0.4% for Si.

Received January 4, 1955

LITERATURE CITED

[1] G. Meyer, "Analysis and Determination of the Structure of Organic Materials" 1935, p. 176; b) E. G. Rochow, An Introduction to the Chemistry of the Silicones, New York, 1951, p. 162.

[2] H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, J. Am. Chem. Soc., 72, 5767 (1950).

[3] E. G. Rochow and W. F. Gilliam, J. Am. Chem. Soc., 63, 798 (1941).

[4] E. G. Rochow and W. E. Gilliam, J. Am. Chem. Soc., 70, 2170 (1948).

[5] A. D. Petrov and V. S. Chugunov, Proc. Acad. Sci., 73, 323 (1950); b) A. D. Petrov and V. F. Mironov, Proc. Acad. Sci., 75, 707 (1950).

[6] M. O. Korshun and V. A. Klimova, J. Anal. Chem., 2, 274 (1947).

[7] M. O. Korshun and N. E. Gelman, "New Methods of Elemental Micro Analysis, State Chem. Press, 1949.

[8] a) M. O. Korshun and N. S. Sheveleva, Proc. Acad. Sci., 60, 63 (1948); b) M. O. Korshun and N. S. Sheveleva, J. Anal. Chem., 7, 104 (1952) (T. p. 121)* ; c) N. E. Gelman and M. O. Korshun, Proc. Acad. Sci., 89, 685 (1953); d) V. A. Klimova, M. O. Korshun and E. G. Bereznitskaya, Proc. Acad. Sci., 96, No. 2 (1954); e) M. O. Korshun, E. A. Terenteva, and V. A. Klimova, J. Anal. Chem., 9, 275 (1954) (T. p. 307)*.

[9] V. A. Klimova, M. O. Korshun, and E. G. Bereznitskaya, Proc. Acad. Sci., 84, 1175 (1952).

[10] V. A. Klimova, M. O. Korshun, and E. G. Bereznitskaya, Proc. Acad. Sci., 96, 81 (1954).

[11] P. P. Fedoseev and M. M. Pavlenko, J. Anal. Chem., 5, 296 (1950); 6, 318 (1951); 8, 158 (1953) (T. p. 175)*.

[12] a) I. Ya. Guretsky, Thesis for Candidate's Degree. The D. I. Mendeleev Moscow Chem. Tech. Inst.; b) A. P. Kreshkov and I. Ya. Guretsky, Trans. Moscow Chem. Tech. Inst., 17, 7 (1952).

[13] M. O. Korshun, J. Anal. Chem., 7, 96 (1952) (T. p. 111)*.

[14] A. P. Kreshkov, V. A. Bork, L. V. Myshleeva, and G. D. Nessonova, "Analysis of Organo-silicon Compounds", State Chem. Press, 1954, p. 171.

[15] K. K. Strelkov, J. Appl. Chem., 26, 1091 (1953) (T. p. 1027)*.

[16] V. A. Klimova and M. O. Korshun, J. Anal. Chem., 6, 232 (1951).

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

NEW METHODS FOR THE QUANTITATIVE DETERMINATION OF HALOGENS AND THE SIMULTANEOUS DETERMINATION OF SULFUR AND HALOGENS IN ORGANIC MATERIALS. PART III

P. N. Fedoseev and N. P. Ivashova

The Nikolaevsk Shipbuilding Institute

Among the numerous methods published in the literature for the quantitative determination of halogens in organic materials, reduction methods occupy a special place; they are advantageously set apart from other methods. Reduction of halogens can be carried out by various methods, e.g.: 1) by nascent hydrogen in a suitable solvent (Stepanov's method [1]); 2) by molecular hydrogen at elevated temperatures in the presence of a catalyst (e.g. Ter-Meilen and Gesling's method [2]); or 3) by heating the organic material with active metals [3, 4] etc.

Alongside Stepanov's method, which has found wide practical application in organic analysis, reduction of halogen containing organic compounds with active metals is gaining more importance. Thus, according to a method developed by M. O. Korshun, M. N. Chumachenko, and V. A. Klimova, organic materials containing halogens are heated with metallic potassium in a steel bomb with a non-screw lid [3]. Complete decomposition of the organic material occurs in this case with formation of the halides and sulfides of the alkaline metals which can be readily determined.

The drawback of this otherwise good method is the necessity of using a metal bomb and working with potassium. We should like to point out that in addition to halogens and sulfur, the alkali metals also react fairly actively, on heating, with nitrogen (especially lithium). In this connection it should be possible to develop new quantitative methods based on the reducing properties of the alkali metals, which would allow the possibility of quantitatively determining the three elements: halogens, sulfur, and nitrogen on one aliquot. We have not come across any published methods for the simultaneous determination of two and three elements on one test aliquot by heating with the alkali metals.

In our earlier work, after analyzing facts already known in the literature [4], and after practical checking, we concluded that by using powdered magnesium metal instead of an alkali metal, it should be possible to carry out a quantitative determination of nitrogen and sulfur [5], easily, accurately, reliably, and fairly quickly. We also pointed out at this time that it should be possible to carry out a quantitative determination of halogens, and also determine the elements indicated, in pairs, on one test aliquot. By using magnesium, there is no need to use a bomb, and certain of the disadvantages of working with an alkali metal are obviated. A small amount of test material is sufficient for analysis. In our own case we analyzed samples ranging in weight from 0.20 to 0.040 g without lowering the accuracy of the quantitative determination of sulfur and halogens.

In this article we have described a method used for analysis of organic materials containing halogens, and halogens and sulfur, respectively. In the quantitative analysis of materials containing halogens and sulfur, sulfuric acid can be used for dissolving excess magnesium metal and for decomposing sulfides and halides. Our fears re the impossibility of using sulfuric acid for decomposing the reaction mass proved groundless (we had thought that under the experimental conditions used, one might have expected reduction of some of the sulfuric acid by magnesium to hydrogen sulfide, which would complicate analytical procedure considerably).

EXPERIMENTAL

1. Determination of Halogens

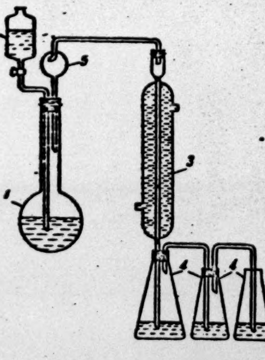
The test aliquot of organic halogen-containing material was placed on the bottom of a glass test tube (or a glass tube fused at one end) 12-15 cm long, and 1-1.5 cm in diameter, and mixed with a small amount of powdered magnesium metal; further amounts of magnesium were then strewn on top so as to fill the tube up to the stopper. The test tube was stoppered with a stopper containing a tube for leading off the gas, and the whole fitted in a specially constructed electric oven [5]. or was heated with a gas burner at 550-650°.

TABLE 1

Experiment number	Designation and molecular formula*	Amount of test material in g	Amount of 0.1 N $AgNO_3$ used in ml	Halogen in %		
				Calculated	Found	Difference
1	Chlorobenzene C_6H_5Cl	0.1316	11.70	31.50	81.52	+0.02
	Chlorobenzene C_6H_5Cl	0.1346	12.05	31.50	31.74	−0.24
2	Dichlorobenzene $C_6H_4Cl_2$	0.1007	13.67	48.24	48.13	−0.11
	Dichlorobenzene $C_6H_4Cl_2$	0.1009	13.67	48.24	48.04	−0.20
3	Dibromobenzene $C_3H_2Br_2$	0.1004	8.49	67.70	67.57	−0.13
	Dibromobenzene $C_6H_4Br_2$	0.0382	3.23	67.70	67.57	−0.13
4	Tribromoaniline $C_6H_8Br_3N$	0.0488	4.43	72.68	72.54	−0.14
	Tribromoaniline C_6H_8BrN	0.0495	4.50	72.68	72.65	−0.03
5	Iodoform CHI_3	0.1004	7.63	96.69	96.44	−0.25
	Iodoform CHI_3	0.1012	7.69	96.69	96.43	−0.26
6	Hexachloroethane C_2Cl_6	0.0996	25.15	89.85	89.63	−0.22
	Hexachloroethane C_2Cl_6	0.0794	20.10	89.85	89.75	−0.10

* Apart from these materials the following compounds were also analyzed: α-chloronapthalene, nitrochlorobenzene, n-chloroaniline, bromobenzene, bromocamphor, tribromophenol, bromoisovalerylurea and sergosine. Experimental error for the compounds just enumerated as well as for those given in the table did not exceed 0.15-0.25%.

Initially, the part of the test tube farthest removed from the test material was heated. Having made a small heated zone, this was gradually increased. Finally the whole tube was heated to a red heat (550-650°), this took 20-30 minutes; it was finally heated for a further 2-3 minutes; heating was then stopped. All the heating process took 20-25 minutes. The cooled tube, rather deformed from heating, was then ground up in a porcelain mortar and transferred quantitatively to a 0.5 liter tall beaker. The mortar was washed out with some distilled water, and the washings added to the beaker. 25-35 ml of 40% sulfuric acid was then added to the reaction mass until all the magnesium had dissolved. The solid residue (carbon, glass) was filtered off. The filter + solid residues were carefully washed with distilled water. To the acid filtrate was added 20-25 ml of 0.1 N silver nitrate, and the halogen content determined by back titration with ammonium thiocyanate. Results obtained for the determination of halogens in organic materials are given in Table 1.



General appearance of the apparatus used for analysis: 1) flask for distilling H_2S; 2) dropping funnel; 3) condenser; 4) receiver; 5) splash head.

2. Simultaneous Determination of Sulfur and Halogens in Organic Materials

The procedure adopted for the simultaneous determination of sulfur and halogens in organic materials was the same as that used for individual determinations of sulfur [5], and halogens.

Test material was heated with magnesium and the final mass transferred to a flask for decomposing and for distillation of hydrogen sulfide.

The first absorption flask for hydrogen sulfide contained 50-60 ml, while the second and third absorption flasks contained 25 ml each, respectively, of the absorption mixture. The mixture was used for trapping the hydrogen sulfide consisted of equal volumes of: 10% zinc sulfate

TABLE 2

Experiment number	Designation and molecular formula of test material*	Amount of test material in g	Amount of 0.1 N I_2 solution used in ml	Sulfur in %		Difference	Amount of 0.1 N $AgNO_3$ used in ml	Halogens in %		Difference
				Calculated	Found			Calculated	Found	
1	Bis(1,1-dimethyl-4-pentenetrione) sulfide, $C_{14}H_{24}O_2S$	0.0798	6.25	12.60	12.55	−0.05	–	–	–	–
	Tetrachlorophthalic acid $C_8H_2O_4Cl_4 \cdot 1/2\,H_2O$	0.0786	–	–	–	–	10.00	45.32	45.11	−0.21
	Total weight	0.1584	–	–	–	–	–	–	–	–
2	Sodium p-toluene sulfonic acid $C_7H_7O_3SNa \cdot 2H_2O$	0.0353	3.10	13.92	14.09	+ 0.17	–	–	–	–
	Tetrachlorophthalic acid $C_8H_2O_4Cl_4 \cdot 1/2H_2O$	0.0204	–	–	–	–	3.75	45.32	45.22	−0.10
	Total weight	0.0647	–	–	–	–	–	–	–	–
3	Sulfosalicylic acid $C_7H_6SO_6 \cdot 2H_2O$	0.0801	6.25	12.61	12.51	−0.10	–	–	–	–
	Hexachloroethane C_2Cl_6	0.0627	–	–	–	–	15.90	89.85	89.91	+ 0.06
	Total weight	0.1428	–	–	–	–	–	–	–	–
4	Bis (1,1-dimethyl-4-pentenetrione) sulfide, $C_{14}H_{24}O_2S$	0.0825	6.40	12.60	12.41	−0.19	–	–	–	–
	Iodoform CHI_3	0.0687		–	–	–	5.23	96.69	96.62	0.07
	Total weight	0.1512		–	–	–	–	–	–	–

---

* Apart from the mixtures of organic materials indicated in the table, various other combinations of materials containing sulfur and halogens were tested. Experimental error did not exceed 0.15-0.25%.

and 10% sodium acetate. Air was expelled from the apparatus by means of carbon dioxide; from a dropping funnel was then added 25-35 ml of 40% sulfuric acid until all the magnesium had dissolved completely. When solutions was complete, the flask was heated to distill off the hydrogen sulfide, the sulfide sulfur being then determined by iodometric titration. After determination of sulfur, the dropping funnel was carefully washed with distilled water, and the wash water combined with the solution in the reaction flask. The contents of the flask were filtered off from solid residue, the solid residue + filter washed with distilled water, etc., and the halogens determined argentometrically in the filtrate. Results for simultaneous determination of sulfur and halogens in one weight of sample are given in Table 2.

SUMMARY

1. Methods are described for the quantitative determination of halogens, and for the simultaneous determination of halogens and sulfur in one aliquot of organic material.

2. Accuracy of the methods lie within the limits of ± 0.2-0.3%.

3. The possibility of using these methods for the determination of small amounts of sample (0.040 g) has been established.

4. When readily volatile materials are being analyzed it is expedient to carry out the determination in a long (20-25 cm) glass tube.

5. During analysis of materials containing sulfur and halogens, it is possible to use sulfuric acid for dissolving the reaction mass.

Received June 29, 1953

LITERATURE CITED

[1] A. Stepanov, J. Russ. Phys. Chem. Soc., 37, 12 (1905); 39, 4056 (1906).

[2] G. Ter-Meilen and I. Gesling, "New Methods of Organic Chemical Analysis", Leningrad 1931.

[3] M. O. Korshun and N. E. Gelman, "New Methods of Organic Chemical Analysis", Moscow, 1949, pp. 88-98.

[4] K. Bürger, 1, 1029 (1942).

[5] P. N. Fedoseev and N. P. Ivashova, J. Anal. Chem., 7, 2, 133 (1952) (T. p. 116)*.

---

* T. p. = C. B. Translation pagination.

DETERMINATION OF THE AMMONIUM ION BY CONDUCTOMETRIC TITRATION

G. B. Pasovskaya

The Turcoman State Institute of Medicine

There are published references to the use of conductometric titration in the work of Kolthoff [1], and Pfundt [2]. These authors give as examples titration of both pure ammonium chloride, and of ammonium chloride in the presence of acids (boric, acetic). All the same, there is no information in these papers as to what concentration of ammonium chloride it is possible to titrate, and about the effect of other ions on the titration results.

As our test material we chose ammonium sulfate, from which, after a three fold crystallization, we prepare a standard solution containing an exactly known weight of ammonium ion per ml of solution. Distilled water freed from carbon dioxide by prolonged boiling was used for making up the solution. This solution was used as a stock solution for preparing other solutions of varying ammonium concentrations, for titration. For this purpose a known volume of the standard solution of ammonium sulfate was measured out into the vessel for conductometric titration by means of a micro-pipet; distilled water was then added to make up the volume to 50 ml. The solution thus prepared was carefully mixed with a piston type cylindrical stirrer and titrated with sodium hydroxide, prepared according to Kolthoff [3]. Addition of reagent to the solution being titrated was made by means of a pneumatic micro-buret; the latter was made from an ordinary 2 ml micro-pipet not graduated right to the end. The tip of the micro-pipet was drawn out into a capillary and bent into the shape of a hook. A rubber tube was fitted on to the top end of the micro-pipet to connect the micro-pipet with a 2 ml syringe (with a glass piston). During titration the bent tip of the micro-pipet should touch the solution being titrated. If the syringe piston fits well and does not pass air, a micro-buret made in this way works very well; reagent can be measured out with an accuracy of thousandths of a ml. It should be pointed out that the electroconductivity of the solution does not change during the time after addition of reagent. Titration was carried out in an apparatus for conductometric and potentiometric titration based on the Toropov system [4]. The shape of the titration curve is shown in Fig. 1.

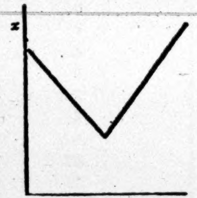


Fig. 1. Graph for the conductometric titration of ammonium with sodium hydroxide.

Table 1 gives examples of determination of ammonium ion by titration with sodium hydroxide of two different concentrations. The sodium hydroxide was standardized conductometrically by titration with solutions of ammonium salts; for convenience of subsequent calculations the number of mls of reagent corresponding to 1 mg of ammonium ions was calculated.

Solutions containing more than 4.5 mg NH_4^+ in 50 ml of solution can be titrated with sodium hydroxide 0.00583 ml of which is equivalent to 1 mg of NH_4^+. Weaker reagent solution should be used for titrating solutions with a lower concentration of the ion to be determined. The smallest amount ammonium ions which we managed to titrate was 0.54 mg NH_4^+ in 50 ml of solution. This determination was carried out using sodium hydroxide, 0.0233 ml of which corresponded to 1 mg of NH_4^+. Fixing the equivalence point is difficult in the case of smaller amounts of ammonium ions.

TABLE 1

Determination of Ammonium Ion Conductometrically with Sodium Hydroxide (Volume of solution titrated ≈ 50 ml)

Experiment number	NH_4^+ taken in mg	NH_4^+ found in mg	Error in %	Observations
1	90	90.05	0.05	Titration carried out with NaOH, 0.00582 ml of which corresponded to 1 mg NH_4^+
2	72	71.35	0.91	
3	54	54.03	0.05	
4	36	36.02	0.05	
5	18	18.01	0.05	
6	9	8.91	1.00	
7	4.5	4.29	4.67	
8	18	18.02	0.05	
9	12.60	12.78	1.42	Titration carried out with NaOH, 0.0233 ml of which corresponded to 1 mg NH_4^+
10	5.4	5.42	0.37	
11	3.6	3.56	1.11	
12	1.8	1.8	0	
13	0.54	0.55	1.85	

TABLE 2

Determination of Ammonium Ions by Conductometric Titration with Sodium Hydroxide, 0.00583 ml of which corresponded to 1 mg of NH_4^+ (Volume of solution titrated ≈50 ml)

Experiment number	Taken			Amount of NH_4^+ found in mg	Error in %
	NH_4^+ in mg	Salt			
		Formula	Amount in mg		
1	36	$NaNO_3$	442	35.68	0.89
1	36	$NaNO_3$	845	36.87	2.41
3	36	KNO_3	622	35.68	0.89
4	36	K_2SO_4	952	36.02	0.05
5	36	KCl	731	36.36	1.00
6	36	Na_2SiO_3	7.2	35.50	1.39
7	36	Na_2SiO_3	14.4	30.87	14.25
8	36	Na_2CO_3	607	35.88	0.34
9	36	$NaHCO_3$	117	35.93	0.20
10	36	$NaHCO_3$	234	35.84	0.45
11	36	$AlCl_3$	403	36.02	0.05
12	36	$AlCl_3$	605	32.59	9.48
13	36	$Ca(NO_3)_2$	682	36.02	0.05
14	36	$Ca(NO_3)_2$	852	34.30	4.73
–	–	$MgSO_4$	262	36.02	0.05
15	36	$MgSO_4$	317	36.87	2.41
16	34.64	$FeCl_3$	36	34.69	0.11
17	34.64	$FeCl_3$	40	41.16	18.82

Note. In experiments Nos. 8, 9, and 10 the solution was neutralized to methyl orange and boiled to remove CO_2.

We also titrated ammonium sulfate solutions in the presence of other ions. From Table 2, which includes results for such determinations, it follows that some ions (potassium, sodium, nitrate, sulfate, chloride) when present in solution up to a certain concentration, do not interfere with determination of ammonium ions. At high concentrations of these same elements in solution, as a consequence of the decrease in relative changes of solution electro-conductivity on addition of reagent, the angle between the branches of the titration curve approaches 180°. This makes exact determination of the equivalence point difficult and leads to an increase in experimental error. SiO_3 ions interfere with determination except at very low concentrations, (Table 2, No. 6). Increasing the content of this ion in the solution being titrated leads to a large experimental error during titration by the method suggested.

For eliminating interference on the part of carbonate and bicarbonate, a definite volume of test solution was neutralized with hydrochloric acid using methyl orange as indicator, the solution boiled for 2 minutes (from the moment when the solution starts to boil), cooled and finally titrated by the method described. In order to carry out titration in the presence of calcium, magnesium, iron, and aluminum, it is essential to add a small amount of dry sodium fluoride to the test solution before titration; the solution is then mixed and titrated by the method suggested. By taking such preliminary measures, it is possible to determine ammonium in the presence of some amounts of the ions enumerated above (Table 2).

On addition of sodium fluoride to test solution which contains, in addition to ammonium, some calcium ions, a precipitate forms which does not interfere with further titration. The equivalence point is easily found in this case. Sodium fluoride added to a solution of ammonium salt containing ferric ions does not form a precipitate. The solution is decolorized as a result of the formation of a complex iron compound, from which sodium hydroxide added during titration, by destroying this compound, precipitates a red-brown precipitate of ferric hydroxide. The titration curve in this instance has the shape shown in Fig. 2. The value of the intercept ab made on the abscissa gives the amount of NaOH used in ml for precipitating iron as the oxide, on the scale used. Intercept bc determines, for the scale used, the number of mls of sodium hydroxide used for titrating ammonium ions. A similar curve is obtained when ammonium salts are titrated in the presence of ferrous ions.

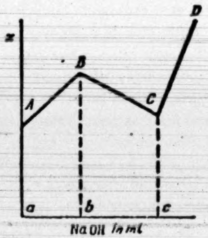


Fig. 2. Curve for conductometric titration of ammonium ions with sodium hydroxide in the presence of the fluoride complex of iron.

On addition of sodium fluoride to a solution of an ammonium salt containing aluminum ions, no precipitate settles out on account of the appreciable solubility of the cryolite formed. On titration with sodium hydroxide, the solution remains clear. The equivalence point is readily determined. Magnesium does not interfere with the determination either when sodium fluoride is present. The method can be used therefore for determination of ammonium ions in the presence of other salts.

SUMMARY

1. A method is suggested for the determination of ammonium ions in the presence of other salts by conductometric titration with sodium hydroxide.

Received May 26, 1955

LITERATURE CITED

[1] Kolthoff, I. M., Z. anorg. allg. Chem., 3, 97 (1920).

[2] Pfundt, O., Ang. Chem., 46, 218 (1936).

[3] Kolthoff, I. M. and Sandell, E. B., "Quantitative Analysis", Third Edition, State Chem. Press, Moscow-Leningrad, 1948, p. 569.

[4] Toropov, A P., Trans. Central Asia State University, 28, 61 (1951).

BLANK
PAGE

POTENTIOMETRIC INVESTIGATIONS ON BARBITURATES

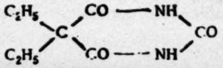
1. THE ANALYTICAL CHARACTERISTICS OF THE SILVER SALTS OF DIETHYL-BARBITURIC ACID (VERONAL)

Ya. M. Perelman

Leningrad Chemico-Pharmaceutical Institute

Barbituric acid derivatives have of late been widely used therapeutically as soporifics. Published methods for their quantitative determination are based mainly on the use of the acid properties of barbiturates. Alkali titration as used in the State Pharmacopeia [1], for Veronal, Luminal and others, using thymolphthalein as indicator, is characterized by the indefinitness of the color change of the indicator, thereby making a decision of the end point difficult. Together with this method, an argentometric method of Budde's [2], is described; this method is based on the formation of a complex with one atom of silver in the presence of sodium carbonate, this complex being soluble in water and not decomposed by carbonates; the author does not give any further details of the chemistry of this method. The method indicated, which has been checked by Babich [3], has found application for control of preparations used for medicinal purposes, when these preparations contain Veronal, Luminal, and some other barbiturates unsubstituted at the nitrogen atom; this method has been used by: Kachalina [4], Perelman and Brodskii [5], for their determination in medicinal preparations. Schulek and Rozsa [6], describe an argentometric method, in which two equivalents of silver are used up per mol of barbiturate to form an insoluble salt; the reactions occur in the presence of borax in a boiling solution. Rozhdestvenskaya [7], Strysowsky and Deverin [8], use the similar reaction of the formation of the disubstituted silver salt in ammoniacal solution as a qualitative micro-chemical test of Veronal. Kicsis and Kovacs [9], precipitate the sodium salt of phenylethylbarbituric acid (Luminal) with silver nitrate, and titrate excess silver with ammonium thiocyanate; they assume in this instance that one equivalent of silver is used per mol of barbiturate. Vaisman [10], describes soluble silver complexes which he isolated, in which one equivalent of silver is used for 1 and 2 mols of Luminal. Danielson [11], reckons that Budde's method is inaccurate and recommends an argentometric method for determining Veronal, which is based on the formation of a complex in the presence of potassium metaborate; this complex has the composition: 1 atom of alkali metal, 1 atom of silver, and 2 molecules of barbiturate. It is clear from what has been said above that the formation of the silver compounds of barbiturates, depend to a significant extent, on many reaction conditions, so that the compound formed varies from case to case, and accordingly affects the accuracy of the methods used. The aim of the present work was to study the conditions under which the silver derivatives of barbiturates, in the first instance of Veronal, are formed, by using potentiometric titration, and to develop a suitable method for the quantitative determination of barbiturates in medicinal preparations.

EXPERIMENTAL

The Veronal used in our experiments (diethylbarbituric acid  molecular weight 184.19) was of a grade which satisfied the requirements of the 8th Edition of the State Pharmacopeia. The purity as established by determining nitrogen by means of a macro-Kjeldhal was found to be 99.65%; we took this value as our starting figure and used it for all our calculations and evaluation of results.

First we dealt with the preparation and characteristics of the insoluble silver salt of Veronal. For this preparation a saturated aqueous solution of Veronal was mixed with a silver nitrate solution to which ammonia had been added beforehand until the precipitate originally formed had redissolved (an appreciable excess of silver nitrate was used). On heating, an insignificant amount of precipitate formed. The solution was filtered, and to the filtrate after addition of two drops of phenolphthalein, was added nitric acid to the neutral point; a voluminous white precipitate was formed at this stage. As subsequent experiments showed, it was found best to prepare the silver salt from Medinal — the sodium salt of Veronal. The precipitate formed was filtered through a glass filter, washed (not for long) with water, then with alcohol, and finally with ether. We should point out that filtration is slow and the precipitate does not become coarser. The final preparation was dried at 50-60° and analyzed for its silver content. Silver was determined as follows: an aliquot of the preparation was dissolved in 20-25 ml of water, to the solution nitric acid was added and the whole heated on a water bath so that the compound was decomposed to reform silver nitrate. On titration of this with ammonium thiocyanate the following percentages of silver were found: 1) 54.73; 2) 54.73; 3) 55.17; 4) 55.10%.

The results do not fully agree with the theoretical value of 54.73%, but they are near enough to indicate that the molecule contains two atoms of silver.

The freshly prepared salt is readily decomposed not only by nitric acid, but even by acetic acid. The following experiments were carried out to determine its solubility: distilled water was saturated with a precipitate of Veronal – Ag_2 under various conditions; 100 ml of the solution thus obtained, after filtration, was evaporated to dryness, and the residue dried at a moderate temperature (50-60°) and weighed. The following results were obtained: 1) S* – $2.41 \cdot 10^{-4}$; 2) S – $1.71 \cdot 10^{-4}$; 3) S – $1.93 \cdot 10^{-4}$. As a mean value we can take $S = 2.01 \cdot 10^{-4}$ mols/liter at 15°. As a check on these results for the solubility of the compound Veronal – Ag_2, it was found possible to calculate it on the basis of the results of potentiometric measurements. For this purpose a cell was made up of the test solution in the presence of the solid phase and a solution of silver nitrate; the electrodes were smooth silver wires 5 cm long; the intermediate solution was a saturated solution of potassium nitrate.

The e.m.f. of the cell $\overset{+}{Ag}$, 0.1 N $AgNO_3$ | KNO_3 | Veronal Ag_2, $\overline{Ag}$; at 15° proved to be 0.142 V. Measurements were made here as in subsequent tests, with a standard potentiometer; a mirror galvanometer served as null-instrument. Using the generally accepted formula:

$$E = 0.0571 \log \frac{0.076}{c_{Ag^+}}$$

(f** for 0.1 N $AgNO_3$ – 0.76; for 0.02 N – 0.87), we get $c_{Ag^+} = 2.50 \cdot 10^{-4}$, from which SP*** is given by

$$\frac{(2.5 \cdot 10^{-4})^3}{2} = 7.8 \cdot 10^{-12}{}^{****}.$$

In another experiment using the cell: $\overset{+}{Ag}$, 0.02 N $AgNO_3$ | KNO_3 | Veronal – Ag_2, $\overline{Ag}$; the e.m.f. was found to be 0.1097.

Using the method of calculating given above we get: $SP = 4.6 \cdot 10^{-12}$. The mean value is given by $SP = 6.2 \cdot 10^{-12}$.

Using this value for the solubility product and the formula $S = \sqrt[3]{\frac{SP}{4}}$, we get $S = 1.10 \cdot 10^{-4}$ mol/liter (the value found in experiments with a saturated solution of Veronal – Ag_2 was $2.01 \cdot 10^{-4}$ mol/liter).

Taking into account experimental difficulties connected with work on silver salts of the given acid (instability of the compound, decomposition during evaporation, poor filtration, etc.) these values can be regarded as being of the same order.

Thus, during precipitation from Veronal solutions, in the presence of excess ammonia, by excess silver nitrate, a disubstituted silver salt of diethylbarbituric acid is formed with a solubility product of $6.2 \cdot 10^{-12}$.

---

* S – Solubility.

** Activity coefficient.

*** SP – Solubility product.

**** In view of the absence of other salts, and the negligible concentration of the Veronal silver compound itself, we omitted its activity coefficient in our calculations.

The following experiments were carried out in order to clarify the character and conditions for direct argentometric titration of Veronal. Solutions of Veronal 0.02–0.06 mol/liter were prepared. 25 ml of solution was titrated with 0.1 N silver nitrate in the presence of 1.0 g of sodium carbonate (anhydrous). The apparatus used for measuring the e.m.f. was the same as that described above. A smooth silver wire was used as electrode. The cell consisted of: Ag — a saturated calomel electrode (in some cases — Ag/Ag) with an intermediate solution of potassium nitrate. Titration was carried out fairly rapidly to start with, 1 ml of the titrant being added, only as the equivalence point was approached was the titrant added in smaller portions of 0.1 ml. Fig. 1 illustrates the type of curve obtained; there is a break at the maximum. In other tests, in order to speed up titration, titrant solution was immediately added in amount only slightly less than that required to get to the equivalence point. Subsequently the portions were cut down to 0.1 ml; after addition of each portion, the potential was measured. As can be seen from the curve adduced, a small, but clearly defined maximum is obtained, which allows the equivalence point to be determined. It is also of interest to note that the appearance of a turbidity which does not disappear, during visual titration, and acts an and end-point indicator, in most cases coincides with the maximum on the ΔE/ΔC curve, which serves as confirmation of the suitability of direct titration of Veronal by silver nitrate in the presence of sodium carbonate. 1 ml of 0.1 N $AgNO_3$ is equivalent to 0.018419 g of Veronal. Table 1 contains the results for titration of Veronal.

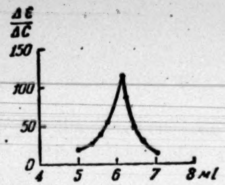


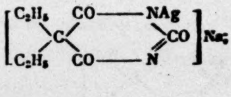
Fig. 1. Titration of 0.021 M Veronal with 0.1 N $AgNO_3$ in the presence of sodium carbonate.

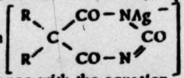
TABLE 1

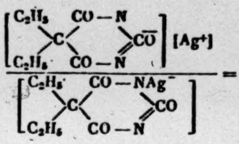
Experiment	Concentration of the solution being titrated	Amount of 0.1 N $AgNO_3$ in ml used for the maximum ΔE/ΔC	Amount of Veronal found in %	Relative error in % (on a 99.65% basis)
1	0.1119/25	5.98	98.39	−1.26
2	0.1119/25	6.09	100.17	+ 0.52
3	0.6480/50	35.1	99.72	+ 0.07
4	0.5286/50	28.5	100.21	+ 0.56
5	0.5495/50	29.9	100.20	+ 0.55
6	0.3455/25	18.65	99.40	−0.25

As is evident from Table 1, experimental error varies within limits up to ± 1.2%. It should be noted that when using large weights of test sample, and the same amount of soda (Experiments 3-5), the maximum is not so clearly defined (ΔE/ΔC = 15, 45, 22), while at the same time in the remaining experiments and under the same conditions, we have ΔE/ΔC = 110, 113, and 120.

As subsequent experiments showed, the potential jump in alcoholic solutions is significantly higher; naturally, this is of practical importance from the point of view of fixing the end point. The amount of soda is not without effect on the stability of the complex, nor consequently on the value of the potential jump. The latter occurs when one equivalent of silver has been used for one mol of barbiturate; from this it can be concluded, that up to the point at which the potential jump occurs, formation of a soluble complex with the composition.



takes place; at the equivalence point, this complex starts to break down. When titration is continued, a second maximum occurs on the curve (but not always) this indicates the end of formation of Veronal–Ag_2. In order to characterize the soluble silver compound of Veronal formed, experiments were carried out to determine the instability constant of the complex anion  . Assuming that decomposition takes place according to the usual scheme in accordance with the equation



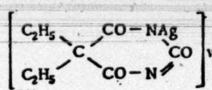
$= K$ instability

we determined this value as follows: Veronal was titrated in a carbonate medium by the classical potentiometric method and some of the points on the titration curve analyzed. Using the usual formula

$$E = 0.0581 \log \frac{0.076}{c_{Ag^+}}$$

the concentration of the silver ion $[Ag^+]$ was calculated from the value of the e.m.f.; on using a saturated calomel electrode (s.c.e.) as the second half-element, calculation of pAg was made on the basis of the formula given by Kolthoff [12] which we corrected for the given electrode and temperature of 20°.

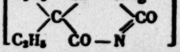
$$pAg = \frac{0.798 - E - 0.2504}{0.0581}$$

The concentration of the complex  was calculated in accordance with the respective point on the basis of the formula $\frac{a \cdot 0.1}{a + b}$ mol/liter, where a designates the number of mls of titrant used (at the test point); 0.1 — is the normality of the silver nitrate solution; b — the number of mls of the original solution; thus a + b is the volume of the reaction liquid at the test point. Veronal concentration was calculated from the formula

$$\frac{(c - a) \cdot 0.1}{a + b} \text{ mol/liter,}$$

where a and b have the same meaning as above, while c — is the number of mls of titrant used to attain the equivalence point (maximum $\Delta E/\Delta C$). We assumed that the activity coefficient of 0.1 N $AgNO_3$ was equal to 0.76*. Insofar as we were calculating the instability of the complex under the given titration conditions, we did not take into account the effect of the carbonate ion on the value of E. The initial carbonate concentration was approximately 0.377 mol/liter. Table 2 contains the results of calculating the instability constant K, based on the analysis of a number of titration curves.

Results of the calculations of K the instability constant of



---

* According to published results, this value relates to a temperature of 25° (but not 20°), but we disregarded this fact as not likely to affect the results of our calculations essentially.

on the basis of an analysis of the potentiometric curves are adduced in Table 2.

TABLE 2

Curves	Number of test points	Mean value of K the instability constant
Curve 1	5	$0.33 \cdot 10^{-7}$
Curve 2	4	$0.48 \cdot 10^{-7}$
Curve 3	2	$0.67 \cdot 10^{-7}$
Curve 4	3	$0.41 \cdot 10^{-7}$

Mean $4.7 \cdot 10^{-8}$ at 20°

This relatively large value of the constant explains why one gets insignificant potential jumps at the equivalent point during potentiometric determinations of Veronal.

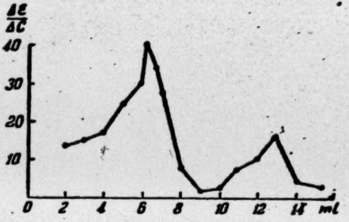


Fig. 2. Titration of 25 ml of 0.026 M Veronal with 0.1 N $AgNO_3$ in the presence of 1.0 N Sodium Carbonate.

And so during the potentiometric titration of Veronal in a carbonate medium (Fig. 2), with silver nitrate, there occurs first of all formation of the sodium salt of argentodiethylbarbituric acid (the section before the first maximum); subsequently the disubstituted silver salt of diethylbarbituric acid (or, using the more correct name, in our opinion, the silver salt of argentodiethylbarbituric acid) is deposited during the stage leading to the second maximum, and finally, precipitation of silver carbonate. Danielson's observation [11], that after the equivalence point (the first maximum) there occurs precipitation of silver carbonate, is wrong, since the precipitate filtered off immediately on the appearance of the first turbidity (or, what is the same, after the first maximum), contained no traces of carbonate. The subsequent path taken by the titration is graphically demonstrated in Fig. 3, where considerably less Veronal and sodium carbonate, approximately a tenth, were taken than in the experiments described above, and in which titration was carried out right up to the end:

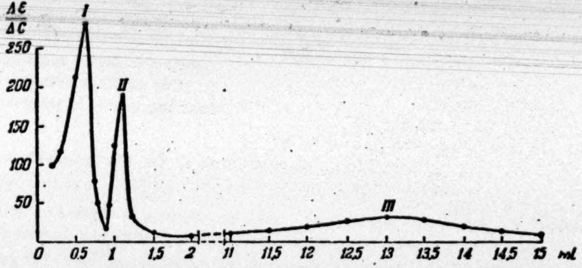
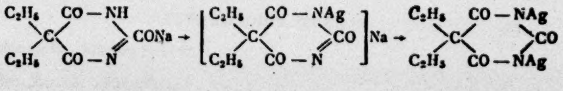


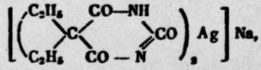
Fig. 3. Titration of 3 ml of 0.026 M/liter of Veronal with 0.1 N $AgNO_3$ in the presence of 0.1 g sodium carbonate: I) [Veronal Ag] Na; II) Veronal Ag_2; III) Ag_2CO_3.

$$[\text{Veronal}\cdot\text{Ag}]\,\text{Na} \rightarrow \text{Veronal}\cdot\text{Ag}_2 \rightarrow \text{Ag}_2\text{CO}_3.$$

The mechanism of the reaction which occurs between Veronal and silver nitrate can be represented by a scheme which we have adduced before [5], during a description of the argentometric method:



Formation of an intermediate complex



similar to that mentioned by Vaisman for the case of Luminal, could not be traced under the potentiometric titration conditions we used. In dealing with the practical value of the method described, one should mention that the potentiometric method widens the scope of the application of the argentometry to barbiturate analysis. Halogens, of course, interfere with the direct argentometric determination of barbiturates; using a potentiometric method however it is possible to determine Veronal (or Medinal — the sodium salt of diethyl-barbituric acid) in the presence, e.g., of bromide by taking only one potentiometric curve. Fig. 4 shows a curve obtained during such a titration: first there is a potential jump which corresponds to the end point for the titration of potassium bromide; the second peak corresponds to Veronal. The accuracy of the bromide determination was up to ± 1%, while for the Veronal it was ± 2%. In the presence of chloride however, when a potentiometric method was used, no separate peaks were observed and only total chloride and Veronal could be determined.

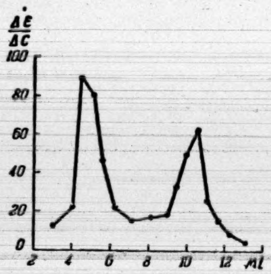


Fig. 4. Titration of 25 ml of 0.0238 M Veronal and 5.1 ml of 0.1 M potassium bromide with 0.1 N $AgNO_3$ in the presence of sodium carbonate.

SUMMARY

1. The possibility has been demonstrated and an actual method worked out for the argentometric determination of Veronal (diethylbarbituric acid) in the presence of sodium carbonate. The error is of the order of 1.2%.

2. On the basis of an analysis of potentiometric curves obtained during titration, the instability constant of a complex which is formed, and which is soluble in water and stable in carbonate solution, has been calculated $K_{\text{instability}} = 4.7 \cdot 10^{-8}$.

3. Direct argentometric potentiometric titration permits determination of Veronal and bromide when these are present together (the experimental error in the case of the bromide is ca. 1%, while for Veronal it is 2%); with chloride present, only total chloride and Veronal can be determined when the same method is used.

4. It follows from an analysis of the potentiometric curves that during titration of Veronal in the presence of sodium carbonate, the turbidity which develops in the result of the formation of a precipitate of Veronal·Ag_2; only when the reaction during which this compound is formed has finished, is a second potential jump observed; after this point carbonate is titrated.

5. A salt of the composition Veronal·Ag_2 has been isolated and its solubility product found to be $6.2 \cdot 10^{-12}$.

LITERATURE CITED

[1] State Pharmacopeia. Edition 8, 1952.

[2] H. Budde, Apt. Z., 49, 295 (1934).

[3] S. Babich, Chem. Z., 4237 (1936).

[4] E. V. Kachalina, Scientific Information Bulletin, Central Pharmaceutical Scientific Research Station, 3, Moscow, 1941, pp. 1-8.

[5] Ya. Perelman and B. Brodsky, "Analysis for Pharmaceutical Preparation", Leningrad, 1950.

[6] E. Schulek, and P. Rózsa, Z. anal. Chem., 112, 404 (1938).

[7] E. Rozhdestvenskaya, Pharmacy 4 (1938).

[8] Strysowsky and Deverin, Chem. Z., 1, 3892 (1934).

[9] E. Kicsis and E. Kovacs, Z. anal. Chem., 124, 40 (1942).

[10] G. A. Vaisman, Author's Thesis for Doctorate, Kiev, 1951.

[11] B. Danielson, J. Pharm. Pharmacol., 3, 7, 435 (1951).

[12] I. Kolthoff and N. Furman, "Potentiometric Titration", Leningrad, 1935.

BLANK
PAGE

PHOTOMETRIC AND COLORIMETRIC DETERMINATION OF THALLIUM AS THE HYDROXIDE OF TRIVALENT THALLIUM

V. K. Zolotukhin and A. S. Molotkova

Lvov State University

Several colorimetric methods have been suggested for the determination of small amounts of thallium, these include: the iodide, thionalide, and sulfide methods, and also turbidimetric and nephelometric methods [1].

We thought it would be interesting to use the formation of $Tl(OH)_3$ for the photometric and colorimetric determination of thallium. Thallium hydroxide has a red-brown color and is capable of forming colloidal solutions. On this basis one of us suggested the salts of trivalent thallium as indicators for determining acids and alkalis [2].

The hydroxide method of determining thallium would appear to be simple and inexpensive, and should permit determination of Tl^{3+} in the presence of Tl^{+} and group 1 cations.

We worked with solutions of $TlNO_3$ of analytical quality, chlorinated to oxidize the thallium. Excess chlorine was removed by drawing air through the solution. A solution of sodium hydroxide was the reagent. Preliminary experiments showed that only solutions of $Tl(OH)_3$ containing not more than 20 γ of thallium in 1 ml are stable. Accordingly, we stabilized colloidal solutions of $Tl(OH)_3$ with gelatine. Gelatine was used as a 1% aqueous solution. 10-20 ml of this gelatine solution was used for 100 ml of the $Tl(OH)_3$ solution. It was difficult to prepare stable colloidal solutions of $Tl(OH)_3$ of higher concentration even on increasing the gelatine content.

Colloidal solutions of $Tl(OH)_3$ were prepared as follows: in an Erlenmayer flask was placed 20-30 ml of water, 10 or 20 ml of a 1% solution of gelatine, and an exactly measured volume of titrant (ca. 0.2 N), a salt of trivalent thallium (the titrant was measured out with a buret). The resultant solution was then transferred to a standard 100 ml flask, diluted with distilled water almost to the mark, and mixed. The foam which was thereby formed was dispersed by addition of 1-2 drops of isoamyl alcohol; the solution was finally made up to the mark.

Solutions prepared in this way were colorimetrically measured in a KOL-1 M photocolorimeter, based on the Vendt system, and photometrically measured on an FM universal photometer (using a light filter No. 8, having γ effective at 436 $m\mu$). We found that excess of sodium hydroxide, and KCl and NaCl, respectively, taken in amounts of 0.1 mol/liter, had no effect on the optical density of thallium hydroxide solutions. We measured optical densities and carried out colorimetric determination of solutions of thallium hydroxide, 10-15 minutes after preparation, although this could also be done 1-2, and even 5 hours after preparation.

Optical densities of solutions containing up to 30 γ of thallium in 1 ml, were measured in a 50 mm cell, those containing from 60-300 γ thallium in a 10 mm cell, and stronger solutions in a 1 mm cell. It was found that the color of $Tl(OH)_3$ solutions containing from 6-180 γ of thallium in a ml, does not fully satisfy Beer's law, while in the concentration range 180-920 γ, the extent of the deviation from this law is less than 1.0%. Accordingly, in the first case, it is necessary to use calibration curves for the photometric determination of thallium. The value which we found for the molar extinction of $Tl(OH)_3$ solutions was 561. The lower limit of concentration for $Tl(OH)_3$ solutions which can still be photometrically measured is $2.4 \cdot 10^{-5}$ mol/liter.

The accuracy and reproducibility of the method we used for photometric determination of thallium as $Tl(OH)_3$ are illustrated by the results given in the table.

Thallium can be determined as thallium hydroxide photocolorimetrically also by using a calibration curve. It is inconvenient to use the technique of doubling during visual colorimetric estimation of thallium as the hydroxide, because of the necessity of getting rid of the foam which is formed after each addition of standard solution; while when the color scale technique is used colorimetric measurement of the thallium hydroxide solutions can only be carried out with freshly prepared standard solutions. When using the method of equations, one should use calibration curves taken for thallium contents of 6-180 γ in 1 ml of $Tl(OH)_3$ solution.

TABLE

Thallium taken, in mg	Experimental error for thallium determination, in % (mean)	Limits of experimental error for thallium determination, in %
6.0	± 2.1	−2.2-+ 2.0
12.0	± 2.3	−2.5-+ 2.0
18.0	± 1.9	−1.8-+ 2.1
30	± 2.0	−1.7-+ 2.5
42	± 1.6	−1.5-+ 2.0

SUMMARY

1. A method is suggested for preparing stable colloidal solutions of $Tl(OH)_3$ with a concentration of up to ca. 1 mg of thallium in 1 ml of solution.

2. Optical density of solutions of $Tl(OH)_3$ containing from 6 to 920 γ of thallium per ml has been measured; it was shown that the color of these solutions does not obey Beer's law exactly.

3. It was found that the molar extinction coefficient of $Tl(OH)_3$ solutions was 561. The lower concentration limit of $Tl(OH)_3$ solutions which can be photometrically measured is $2.4 \cdot 10^{-5}$ mol/liter.

4. Colloidal solutions of $Tl(OH)_3$ can be used for photometric and colorimetric determinations of thallium.

5. Tl^{3+} can be determined by the hydroxide method in the presence of Tl^{+} and cations of the alkali metals.

Received November 23, 1954

LITERATURE CITED

[1] E. B. Sandell, "Colorimetric Determination of Metal Traces", State Chem. Press, 1949, pp. 476-481.

[2] V. K. Zolotukhin, Factory Labs., 2, 133 (1940).

BRIEF COMMUNICATIONS

A COLOR REACTION FOR CYANIDES

V. P. Fedotov

The reaction to be described is based on the formation of a red dye of the polymethine series. which had a yellow fluorescence, by the interaction of cyanogen chloride with anabasine, and aniline. The dye is readily soluble in organic solvents (benzene, chloroform, and dichloroethane).

Chloramine is used as a source of active chlorine, while the carrier of the pyridine ring is anabasine silicon fluoride ($C_{10}H_{14}N_2 \cdot H_2S; SiF_6 \cdot H_2O$). The latter was prepared according to Sokolov's method [1].

To 5 ml of solution to be tested for cyanide contained in a test tube is added 1-2 drops of a saturated aqueous solution of chloramine and 0.2-0.3 ml of a solution of anabasine silicon fluoride (7 parts by weight of salt in 20 parts of water). The solution should be neutral to litmus. If the solution is acid, it should be neutralized with 20% sodium carbonate, while it is is alkaline, 15% tartaric acid solution is used for neutralization. To the neutral solution is added 0.25-0.5 ml of a saturated aqueous solution of aniline and the whole left for 5 minutes, after which 3-4 drops of sodium carbonate is added until the solution is definitely alkaline. In the presence of cyanides (for concentrations not greater than 100 mg/liter) a yellow color which develops before addition of carbonate gradually changes to red with a yellow fluorescence; after 5-20 minutes this color reaches its maximum intensity. If cyanide concentration is greater than 100 mg/liter, the red color may appear even before addition of sodium carbonate. To extract the dye, 1 ml of benzene, toluene, or chloroform is added to the test tube and the contents gently shaken. The colored product goes over completely into the solvent layer. No color appears in the absence of a cyanide.

The amounts of reagents given above give good results for cyanide concentrations in the range 20-100 mg/liter. For greater or smaller amounts of cyanides respectively, the amount of the solutions should be changed accordingly.

The limit of identification is of the order of 0.4 mg/liter. The reaction is specific under the conditions indicated. Iodides interfere.

Received May 12, 1954

LITERATURE CITED

[1] A. V. Sokolov, Trans. of the Sci. Inst. on Fertilizers and Insecto-fungicides, No. 135.

BLANK
PAGE

DETECTION OF THE CADMIUM ION BY A FRACTIONAL METHOD

N. S. Shub

Kiev Polytechnical Institute

The cadmium ion is most conveniently detected in acid media in the form of the sulfide which has a yellow color. All the cations of the IV and V analytical groups however interfere with this reaction. Powdered iron metal, which is normally only used during systematic analysis for separating copper from cadmium [1], can be used for removing them.

Metallic iron hardly reduces cadmium at all; this is easily explained by the fact that the normal oxidation potentials of the systems $Fe^{2+}/Fe = -0.44$ V and $Cd^{2+}/Cd = -0.40$ V [2], have similar values. Iron does not reduce in the presence of nitrate ions or of silver and lead. Nevertheless, the silver ions can be readily removed as the chloride, while lead can be removed as sulfate.

Quadrivalent tin is reduced by iron to the divalent state, but, in the presence of sufficient nitrate ions, on boiling with iron powder it is completely precipitated as the result of an increase in pH. All the other cations of the IV and V groups are quantitatively reduced by iron.

Cadmium is detected by a fractional method as follows: into a test tube is introduced ca. 3 ml of a mixture containing group IV and V cations (except arsenic), and 0.1-0.3 g each of solid KCl, K_2SO_4, KNO_3, and about 0.5 g of powdered iron added.

The mixture is boiled for ca. 1 minute (so that the rising foam washes the solution from the upper side of the tube). The hot mixture is filtered through a small filter. To 2 ml of the clear filtrate is added 2 ml of 1 N HCl and 2 ml of water freshly saturated with hydrogen sulfide. In the absence of cadmium ions, no turbidity develops (sometimes a small amount of whitish turbidity caused by free sulfur appears). When cadmium is present, then immediately, or after a few minutes (depending on the cadmium concentration) a yellow precipitate is formed, or a yellow or sometimes yellow tinged with brown turbudity of cadmium sulfide appears. If there is only an insignificant amount of turbidity, a blank should be carried out.

The limit of identification is 100 γ Cd in 2 ml of filtrate; the limiting dilutions is 1 : 20,000; detection takes 2-3 minutes.

Received June 19, 1954

LITERATURE CITED

[1] V. N. Alekseev, "Qualitative Analysis", State Chem. Press 1951, p. 261.

[2] V. I. Perelman, "Concise Chemist's Notebook", State Chem. Press, 1951, p. 446.

BLANK
PAGE

REVIEW

Electrometric pH Determinations. Theory and Practice. Roger G. Bates. xiii + 331 pages, J. Wiley and Sons, New York; Chapman and Hall, London, 1954.

Electrometric methods of pH determinations are widely used in scientific-research laboratories and for industrial control. There are many well known examples of the use of pH measurements for acid-base titration, in the study of the composition and stability of complex compounds, in the investigation of basic salt formation, methods of fractional precipitation, oxidation-reduction, biochemical, and other reactions. pH measurements are of great importance in understanding and controlling soil, physiological, and technological processes.

The monograph under review was written in consideration of the modern achievements of electrochemistry and is devoted exclusively to electrometric methods of pH determination; its author, Doctor Bates, is known for his works in the field of electrode potentials and homogeneous equilibria, thermodynamics of electrolyte solutions, pH-measurement standardization and the dissociation of weak acids and bases. The first six chapters of the book (155 pages) contain a discussion of the theoretical and experimental bases of the practical electrometric scale of acidity and a comparison of the different scales with each other. The last four chapters (157 pages) are devoted to experimental methods of pH determination.

After establishing the basic concepts (Chapter 1), in the second chapter the author compares the different acidity scales.

In the next chapter the ionic diffusion potentials and activity coefficients are considered in detail, as is calculation of the diffusion potentials on the basis of the well known propositions of MacInnes and Guggenheim, and a method is given for their experimental determination. Special attention is given to methods of eliminating the potential at the liquid-liquid interface. For a number of cases pH determination results are given on utilization of cells with and without a liquid compound. In the same chapter there is a brief discussion of the effect of the residual diffusion potential on the results of pH measurements using standard solutions for comparison.

Chapter 4 is devoted to standards and their utilization for periodic regulation of the standard potential of the indicator electrode. Here there is a detailed description of the method of Con, Geirot and Menkin, based on the dependence of the magnitude of the standard potential on the logarithm of the dissociation constant of the acids of buffer mixtures. On the basis of his own experimental data, the author considers the dependence of standard potentials on the ionic strength of the solution. This same chapter also discusses the well known work of MacInnes, Belcher and Shedlovsky, which led to the establishment of the practical scale for pH measurements which needs no correction for the diffusion potential. Various buffer mixtures are recommended as standards, the pH of which is determined by the e.m.f. method. The properties of phthalate, borate, tartrate, tetroxalate and other buffer mixtures are considered in detail and the dependence of their pH on the method of evaluating the activity coefficients shown. The considerations of the author on the possibility of using the results of pH determination for calculating thermodynamic dissociation constants are of great interest.

Chapter 5 covers generally known concepts of the mechanism of buffer action, buffer capacity, and the effect of dilution on the pH of solutions of strong acids, bases and buffer mixtures. The author's concept of the effect of dilution on ionic activity coefficients is especially valuable. Much attention is given to the salt effect and the effect of temperature on the pH value. The effect of pressure on the pH of solutions of weak acids or bases is considered. The chapter concludes with a brief review of the practical applications of buffer solutions and citation of a number of buffer mixtures that have a high capacity in an extended pH range or are distinguished by constant ionic strength at various pH.

Chapter 6 is perhaps the most interesting one in the entire monograph. Holding with the theory of Bronsted-Laury, the author emphasizes the anology between oxidation-reduction and acid-base reaction, and introduces the concept of acid potential as the basis for comparison of the acidity of solutions in different solvents. Considerable attention is given to the effect of the dielectric constant on the course of protolytic reactions (the effect of the dielectric constant on the ionic activity coefficients, magnitudes of the dissociation constants, activity of protons, and salt formation). For determination of the pH of concentrated solutions of strong acids, for example sulfuric, the author describes the method of Michaelis and Granik, which is based on the dependence of the difference of normal oxidation-reduction potentials of the lowest and highest degree of oxidation of certain dyes on the pH value. The chapter concludes with a detailed discussion of the methods and results of determining the acidity of solutions in anhydrous CH_3COOH. A special section is devoted to practical questions of determining the acidity in non-aqueous mediums in general.

Chapter 7 briefly presents the theory of, and describes methods of using, hydrogen, quinhydrone, antimony and also tungsten, chloranil, pyrolusite, and oxygen electrodes. In this chapter a brief description is given of the action mechanism of the glass electrode, and its most common designs are presented. Considerable attention is given to the preparation of the calomel electrode; there is a detailed discussion of the effect of the physical structure of the interface between the salt bridge and the solution being tested on the reproducibility, constancy and magnitude of the diffusion potential. Pointing out the most important sources of error in the utilization of calomel electrodes and methods of eliminating them, the author gives standard e.m.f. values for a number of cells constructed with this electrode. The Ag-AgCl electrode is discussed. The chapter concludes with a discussion of the effect of the pH on the magnitude of the temperature coefficient of the electrode potential and the e.m.f. values of voltaic cells.

Well deserved space – all of Chapter 8 – is devoted in the monograph to the glass electrode. The following problems are considered here: the difference in the sensitivity of the hydrogen and glass electrode, the structure of electrode glass, the effect of the hygroscopicity of glass on the sensitivity of the electrode, the effect of the chemical stability of glass on the results of pH determination, electrical resistance of the glass electrode, the development of an asymmetrical potential and its measurement, the composition of electrode glass, the errors of the glass electrode, its behavior in non-aqueous solvents, inner comparison electrodes, and the characteristics of commercial glass electrodes. The chapter concludes with a discussion of general rules for using glass electrodes.

Chapter 9 considers the practice of measuring e.m.f. The characteristics of the basic instruments used for measuring e.m.f. are given; potentiometers, galvanometers, the common Weston photometer, and the circuit diagrams of several pH meters of American and European origin are given. Moreover, in Chapter 9, the effect of moisture and temperature on pH measurement by means of pH-meters is discussed, and the basic operational principles of these instruments are described. In conclusion there is a brief description of the design of automatic titrators.

Chapter 10 describes the principles and basic instruments for automatic pH regulation. The chapter concludes with a brief description of an apparatus for industrial pH regulation.

At the end of the book there are 6 tables and an author and subject index.

The work contains about 600 references to literature sources. In the main, the bibliography embraces the most important publications from the date of appearance in print of the first works of Zerensen (1909-1953, inclusive). For certain chapters the literature is cited so completely (Chapters 2, 4 and 8) that they represent reviews in themselves. It is vexing, however, that in his detailed bibliography the author did not mention the excellent monographs of Soviet scientists: the book by V. A. Pchelin "Measurement of Hydrogen-Ion Activity with the Glass Electrode", the book by S A. Strelkov "Analysis and Automatic Regulation of pH", etc. Although the author refers to a number of works by Soviet scientists (N. A. Izmailov and associates, A. I. Pasynsky, B. P. Nikolsky, V A. Pchelin, V. A. Pleskov, S. I. Sokolov, A. A. Smirnov, P. A. Kryukov and E. A. Yanevsky), the bibliography in this respect is incomplete. Among the defects of the work is the lack of focus and concision in the description of the practical value of pH measurements.

Despite the defects cited, the appearance of Bates' book may be considered an important event in chemical literature. The high theoretical level of the book, the strict thermodynamic discussion of the problems associated with pH, the systematic application of the Bronsted-Laury theory to the determination of the acidity in non-aqueous solvents, the detailed description of experimental methods of electrometric pH measurement, and the precise clarity of exposition are positive aspects of Bates' monograph.

The reviewed book is of great interest for analytical chemists, researchers and engineers who use electrometric measurement or pH regulation.

The appearance of a Russian translation would be greeted with interest by numerous Soviet readers.

A. I. Busev and N. G. Polyansky

BLANK
PAGE

CHRONICLE

CONFERENCE ON SPECTROPHOTOMETRIC AND COLORIMETRIC METHODS OF ANALYSIS

The All-Union Conference on Spectrophotometric and Colorimetric Methods of Analysis, called by the Commission on Analytic Chemistry and the Institute of Geochemistry and Analytical Chemistry of the Acad. Sci. USSR, met in Moscow on December 15-17, 1955.

Four hundred persons, representatives of 230 scientific institutes of the Academy of Sciences, scientific-research institutes of various ministries, institutions of higher education, and factory laboratories were present at the conference.

The purpose of the conference was the exchange of knowledge of Soviet scientists in the field of the theoretical problems and practical applications of spectrophotometric and colorimetric methods of analysis, and discussion of the further development of this field of analytical chemistry. There was a total of 38 reports presented.

Two main groups of questions were considered at the conference.

1. Application of spectrophotometric and colorimetric methods for study of the processes of complex formation in solutions, the possibility of utilizing these methods for establishing the structure of molecules, and determining the composition and dissociation constants of complex compounds.

2. Application of spectrophotometric and colorimetric methods for identifying substances by absorption spectra, for determining small concentrations of substance, and for determining organic compounds with the utilization of the infra-red region of the spectrum.

M. V. Savostyanova in her report reviewed the current light-absorption methods and discussed perspectives for their development.

I. V. Tananaev reported the results of his work on the study of gallium compounds with oxalic and tartaric acids in solutions by the method of physico-chemical analysis. Utilization of the ultra-violet region of the spectrum permitted the author to work with colorless solutions.

The report of A. K. Babko concerned spectrophotometric methods of determining the dissociation constants of complex compounds. The author showed the practical value of this physico-chemical criterion for the selection of optimal conditions of spectrophotometric and colorimetric determinations of elements.

N. P. Komar showed the peculiarities and possibilities of spectrophotometric and colorimetric methods of analysis for determining the composition of complex compounds, their dissociation constants and molar extinction coefficients.

K. B. Yatsimirsky clarified the question of the theory and practical application of the kinetic method of analysis, which makes possible the utilization of catalytic reactions in spectrophotometric analysis for the determination of small quantities of elements.

In his survey report V. I. Kuznetsov described methods of raising the sensitivity of colorimetric reactions. Color reactions were discussed on the basis of the chromophoric action of elements, on the basis of complex formation, kinetic and oxidation-reduction reactions.

The reports of Yu. I. Usatenko and E. A. Klimkovich, V. I. Tolmachev and L. N. Serpukhova, V. I. Kuznetsov and A. A. Nemodruk were devoted to the determination of small concentrations of Zr, Hf, Co, and Cr.

The report of V. M. Peshkova showed that investigation of the absorption spectra of both reagents as well as of the resulting compounds permits correct selection of the optimal conditions for colorimetric determination of the elements.

A. T. Pilipenko discussed the relation of the absorption spectra of compounds of elements and reagents containing thionic and thiolic groups to their stability and to the position of the elements in the periodic system of elements.

Two reports, those of Z. F. Shakhova and R. K. Motorkina and of A. I. Kokorin, were devoted to the application of heteropoly acids to chemical analysis.

In the first report it was shown that the nature of the central, complex-forming atom does not affect the character of the spectrum. Replacement of molybdenum by vanadium in the addend displaces the light-absorption maximum to the visible portion of the spectrum. This phenomenon was employed by the authors to design a colorimetric method of determining germanium. A. I. Kokorin suggested the use of heteropoly acids with mixed addends that he synthesized for determining reducing agents.

Several reports were devoted to the utilization of the infra-red region of the spectrum for the analysis of hydrocarbons.

Reports by A. S. Toporets and Z. F. Zhidkova on methods of spectrophotometry for light-dispersing mediums, and by N. S. Poluektov and K. I. Ivanov on the application of flame photometry were also heard at the conference.

The conference noted that spectrophotometric and colorimetric methods of analysis are continuing to develop successfully and that in recent years a number of very valuable theoretical and practical results were achieved.

The great need for rapid and accurate methods of determining small quantities of substances without preliminary separation and determination of the degree of purity of the different substances encouraged the development of these methods; on the other hand, development and broader application of these methods has become possible due to the manufacture of a number of invaluable new instruments by the national industry.

However, despite the success attained in the dissemination of methods of spectrophotometry and colorimetry, there are a number of factors checking the development of these methods and their utilization. The laboratories of factories, geological departments and institutions of higher education are as yet insufficiently equipped with new apparatus for spectrophotometric and colorimetric analysis. There is still insufficient research on the properties of complex compounds and the determination of their composition via the methods of physico-chemical analysis. Only for a small number of compounds of individual elements with organic reagents have the absorption spectra been investigated; this does not permit correct evaluation of the optimal conditions for determining the elements. Research is slowly proceeding on the application of spectrophotometric methods to analysis of industrially important organic compounds.

The conference passed a number of resolutions on problems concerning the development of spectrophotometric and colorimetric methods and their practical application, on the manufacture of instruments and reagents, and also on the publication of the corresponding literature.

With respect to questions concerning the development of the theory of spectrophotometric and colorimetric methods and their practical application, the conference recommended, for successful application of spectrophotometry in the field of analysis of organic and inorganic substances, the diligent development of research on various equilibrium systems from the point of view of the theory of ionic equilibria, and also it recommended further development of the theory of organic reagents, directed toward the discovery of more highly sensitive reactions.

Utilizing the advantages of the spectrophotometric method, it is necessary to determine the conditions for analysis of multicomponent systems without preliminary separation of the complex mixtures.

It is necessary to stimulate research on the composition, dissociation constants, and other properties of complex compounds via methods of physico-chemical analysis. Special attention must be given to the development of methods for determining microquantities of elements and compounds, which is very important in the preparation of metals with a high degree of purity, and substances and reagents of analytical grade. It is necessary to develop research on the theory and practice of kinetic methods of analysis and, in particular, more widely to utilize catalytic reactions for the determination of small quantitites of elements in spectrophotometric analysis.

It is necessary to expand systematic spectrophotometric research on compounds of elements with organic reagents, giving special attention to the determination of rare elements. It is necessary to carry out systematic research on the precise measurement of absorption spectra in an extended wave-length range of the reagents and the resulting colored and colorless compounds used in analysis, in order to prepare for publication a suitable compilation of spectra.

In the investigation of new and the approval of present variants of spectrophotometric analysis it is necessary more widely to utilize methods of statistical analysis and to specify more strictly the conditions under which analysis is carried out. More attention must be given to the development of methods of flame photometry and especially to the quantitative determination of alkali and alkali-earth elements. It is necessary to develop the theoretical and applied aspects of fluorometric methods of analysis of organic and inorganic compounds.

It is necessary to expand scientific research on the application of methods for the spectrophotometry of dispersion mediums and to find practical applications for these methods. It is necessary diligently to develop research on the design of automatic instruments.

In the section concerning the manufacture of instruments, the conference recommended increasing the production of SF-4 spectrophotometer with appropriate modernization, and noted that in addition to this instrument it is desirable to have precision instruments with high resolving power and spectral clarity for spectrophotometric work work in the determination of physico-chemical constants.

The conference pointed out the necessity of turning out in larger quantity photoelectrocolorimeters of the type FEK-N 52 with the necessary improvements, and of organizing mass production of simplified spectrophotometers with interference light filters for the whole length of the spectrum, as well as mass production of an apparatus for the measurement of fluorescence in liquids, with accessories for titration and apparatus for luminescence analysis. It was declared desirable to accelerate the production of flame photometers with interference filters.

The conference considers it necessary to increase considerably the production of a wide assortment of better quality reagents, especially organic reagents and salts of rare elements; and to include in the 1956 plan and the next Five-Year Plan the preparation of reagents in accord with the list approved by the Commission on Analytic Chemistry and the Institute of Chemical Reagents.

The Conference resolved to ask the Ministry of Ferrous Metallurgy to enlarge the assortment of standard specimens of ores, alloys and pure metals for plotting calibration curves and for regulating the accuracy of analysis.

In the field of publications the Conference resolved to ask the State Chemistry Press to publish the monograph of A. K. Babko and A. T. Pilipenko on colorimetric and spectrophotometric methods of analysis with appropriate additions and changes; to advance the publication data of the monograph of N. S. Poluektov on flame photometry, of the monograph on spectrophotometric analysis of organic substances, and the text on luminescent analysis. Moreover, it was declared desirable to have the Institute of Scientific Information of the Acad. Sci. USSR publish periodic reviews on questions of spectrophotometry and colorimetry.

BLANK
PAGE

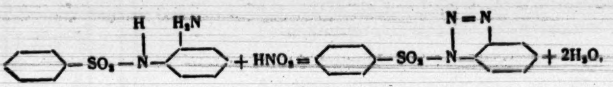
A NEW GRAVIMETRIC METHOD FOR THE DETERMINATION OF THE NITRITE ION USING NITRITON-B (o-AMINOANILIDE OF BENZENESULFONIC ACID)

N. P. Komar and I. Yu. Martynchenko

A. M. Gorky Kharkov State University

During studies of the interaction of NO_2^- ions with the o-aminoanilide of benzenesulfonic acid, which we tried to use instead of the less readily available o-anilide of diphenic acid (Nitriton A) [1], it was found that the white turbidity, which appears on pouring the solutions together, very rapidly changes over into a coarse crystalline precipitate. In this sense, Nitriton B behaves like substances whose solubility changes considerably with crystal size, while the white turbidity which Nitriton A forms with nitrite ions, does not possess this property.

Preliminary experiments showed that Nitriton B practically completely precipitates NO_2^- ions according to the reaction



leading to the formation of benzenesulfanyl-o-phenylenediazimide (atriazole). This precipitate, as indicated above, satisfies the requirements normally met in gravimetric analysis. This fact persuaded us to study the possibility of using this reaction for the direct gravimetric determination of nitrite. This problem proved of particular interest in view of the fact that hitherto no method has been published for the gravimetric determination of nitrite ions.

$NaNO_2$ Solution. The solution was prepared from chemically pure grade material, which was given a preliminary wash with boiled water; it was isolated from air by means of two washers, one of which contained a solution of KOH 1 : 2, while the other contained a mixture of one volume of KOH 1 : 2 and one volume of pyrogallol 1 : 5. NO_2^- concentration was checked by means of permanganate.

Nitriton B Solution. 2.480 g of the o-aminoanilide of benzenesulfonic acid was dissolved in 1 liter of 0.2 M H_2SO_4. The solution can be stored.

All the dilutions were carried out in calibrated measuring apparatus to ensure errors of not more than 0.2%.

Preliminary tests were carried out over a wide pH range for 3.0 to 8.5. It was found that at a pH of 8.5, in general, no precipitate of the triazole was formed; neither was any formed at lower pH values until 3.5 was reached, at which it was first detected. Within this pH range the reaction for NO_2^- remained quite positive. Only at a pH of ≤ 3 was quantitative separation of NO_2^- ions from solution achieved; at a pH of ≤ 1.5 however, together with precipitate formation, the odor of nitrogen oxides could be detected, indicating the danger of loss of NO_2^- ions. In this connection, further work was carried out in the pH range 1.5-2.8, with slow addition of reagent to the solution to be tested and efficient agitation. It was found, in addition, that complete precipitation of NO_2^- ions was achieved when 1.5 moles of Nitriton B was used per 1 g-ion of NO_2^- ions. When all these conditions were satisfied, precipitation was complete in 10-15 minutes.

Determination of nitrite ions in solution was carried out as follows. A known amount of $NaNO_2$ solution was pipetted into a 100 ml beaker, and Nitriton B solution added dropwise. In order to maintain the pH at 1.5 - 2.8, the solution was diluted with water and the necessary amount of 1 M Na_2CO_3 solution added. The total volume of solution in all tests was about 75 ml. After standing for 8 hours in the dark, the precipitate was filtered off in a sintered glass crucible No. 4. The precipitate was washed with 5-10 ml of 0.1 M H_2SO_4, then 6 times with cold water, and dried to constant weight in the apparatus shown in Fig. 1, which was fitted up in a drying oven heated to 75°. As can be seen from Fig. 1, crucible 1 is fitted in a hole cut in a rubber plug 2 and is covered with a glass adapter 3, in the spherical bulb 4 of which is fitted a plug of glass wool. A calcium chloride drying tube is fused directly on the adapter 3, this tube being filled with calcium chloride and stoppered with plug 6, through which passes a tube 7 connected to a large column filled with $CaCl_2$ located outside the drying oven. To the end of the air outlet tube 8, sticking out of the drying oven is fitted a Drechsel bottle containing sulfuric acid which could be used as a bubble counter. In operation air was sucked through at the rate of a bubble per second. Using such an apparatus, the precipitate could be dried in 20 minutes instead of 1.5 to 2.0 hours which would be spent if drying were carried out using ordinary drying conditions in a drying oven.

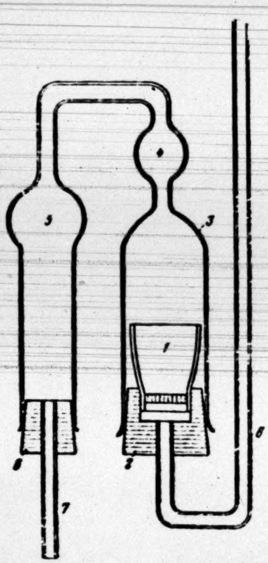


Fig. 1. Apparatus for drying the precipitate.

Experimental results which have been treated statistically [2], are given in Table 1, the reliable level was $\alpha = 0.95$; they were calculated by means of the stoichiometrically obtained conversion factor $F = 0.1774$ ($\log F = \bar{1}.2491$). As is evident from Table 1, the method gives completely satisfactory results.

Qualitative tests showed that in the pH range 3.5 to 1.0, within which limits the NO_2^- ion is precipitated, Nitriton B only forms white crystalline precipitates with Ag^+, Hg_2^{2+} and Hg^{2+}.

When such oxidizing agents as MnO_4^-, $Cr_2O_7^{2-}$, IO_3^-, $S_2O_8^{2-}$ and Fe^{3+} were tried out against Nitriton B, and ClO_3^- solutions both in the cold and on warming, an orange color developed when large amounts of the oxidizing agents were present, and a rose color when small amounts were present. High concentrations of oxidizing agent gave on heating a dark orange precipitate, which on further oxidation, became paler, maintaining a yellowish color. In alkali media, oxidizing agents color the Nitriton B solution differently, from yellow-green to cherry-red. On acidification of an alkaline solution, the yellow-green color changes to red-orange. The transition range extends from pH 5.2 to 5.6.

TABLE 1

Gravimetric Determination of NO_2^- by Means of Nitriton B

NO_2^- taken in mg	Number of determinations	NO_2^- found in mg $\bar{c}$	$\Sigma (c_i-\bar{c})^2$	s^2*	$s_{\bar{c}}$**	$t_{0.95} \cdot s_{\bar{c}}$
10.0	10	10.05	0.110	$1.1 \cdot 10^{-2}$	$3.5 \cdot 10^{-2}$	±0.08
15.0	10	15.02	$3.4 \cdot 10^{-2}$	$3.4 \cdot 10^{-3}$	$2.0 \cdot 10^{-2}$	0.04
20.0	10	20.04	$6.9 \cdot 10^{-2}$	$6.9 \cdot 10^{-3}$	$2.8 \cdot 10^{-2}$	0.06
30.0	10	30.07	0.168	$1.7 \cdot 10^{-2}$	$4.3 \cdot 10^{-2}$	0.10

---

* $s^2 = \dfrac{\Sigma(c_i - \bar{c})^2}{n}$. ** $s_{\bar{c}} = \dfrac{s}{\sqrt{n-1}}$

Thus, it seems that Nitriton B may be regarded as a specific precipitating reagent for the nitrite ion, since Ag^+, Hg_2^{2+}, and Hg^{2+} ions are rarely met with at the same time as NO_2^- ions.

Further studies of the properties of the triazole precipitate showed that it will withstand temperatures not exceeding 75° for long periods without changing weight or outward appearance. At 90–110° the white crystals of the triazole gradually acquire a rose color and then become orange; simultaneously the weight increases. This precipitate partially dissolves in water to give a red colored solution. The white residue which is insoluble in water is the normal triazole; it does not dissolve in 0.1 M H_2SO_4 but dissolves completely in 0.1 M NaOH; on subsequent acidification of the alkali solution, no precipitation occurs. Solutions of triazole in sodium hydroxide have the following properties: on heating, or long standing, they become yellow if the triazole concentration is low; oxidizing agents (CrO_4^{2-}, IO_3^+) also color them yellow; on oxidation of triazole solutions acidified beforehand, a rose color develops. The capacity of triazole to give colored products on oxidation was used for the colorimetric determination of its solubility in water.

A calibration curve was constructed: 0.2590 g triazole was dissolved in 50.00 ml 0.1 M NaOH with gentle warming; the solution was neutralized with H_2SO_4 and diluted with 0.1 M H_2SO_4 to 1 liter; triazole concentration in this first solution was $1.00 \cdot 10^{-3}$ M/liter; 25.00 ml of first solution was diluted with same solution of 0.1 M H_2SO_4 to 500 ml; the concentration of this second solution was $5.00 \cdot 10^{-5}$ M/liter; aliquots of this second solution were measured out by means of a micro-buret into a 50 ml flask, 5 ml of $5.0 \cdot 10^{-3}$ M KIO_3 added, and the volume made up to 35 ml with 0.1 M H_2SO_4; this solution was heated 5 minutes, allowed to stand 12 hours in the dark at room temperature, made up to 50 ml with water, and the optical density measured on an FEK-M colorimeter.

The calibration curve proved to be a straight line:

$$c = 1.925 \cdot 10^{-6} + 1.373 \cdot 10^{-4} D,$$

where c is the desired triazole concentration, while D is the corresponding optical density.

Determination of the solubility of triazole in water was carried out as follows: an aliquot of the Nitriton B solution was precipitated with a small excess of $NaNO_2$ solution; the precipitate was washed first with 0.1 M H_2SO_4 to a negative reaction for NO_2^- ions, then with water to remove SO_4^{2-} ions; the washed precipitate was transferred to a flask to which was added 500 ml of water, and the whole allowed to stand in the dark with frequent agitation; after 5 days, 250 ml of filtrate was taken and evaporated on a water bath to ~ 30 ml, which was transferred to a 50 ml standard flask; 5 ml of $5.0 \cdot 10^{-3}$ M KIO_3 solution prepared in 0.1 M H_2SO_4 was added, and after a five minute heating on a boiling water bath, the solution was left for 12 hours in the dark at room temperature; after dilution of this solution to the mark (50 ml) with water and mixing, its optical density was measured photocolorimetrically and the triazole concentration determined by means of the graph. The solubility of triazole determined in this way by 10 measurements was found to be equal to

$$(3.0 \pm 0.3) \cdot 10^{-6} \text{ M/liter},$$

at a reliable level of 0.95; this corresponds to a loss of 0.138 mg NO_2^- ion per liter of solution.

Two further series of tests were carried out to ascertain the errors arising on precipitation of the triazole in the presence of other ions. Results of these tests are given in Table 2, where Series No. 1 includes determinations of nitrite ion in a solution, 1 liter of which contained at the same time $1.0 \cdot 10^{-2}$ M solutions of each of the nitrates of zinc, cadmium, magnesium, manganese, aluminum, and potassium; while Series No. 2 included determinations in a solution, 1 liter of which contained at the same time $1.0 \cdot 10^{-2}$ M solutions of Na_3AsO_3, Na_2HPO_4, $Na_2B_4O_7$, KCNS, NaBr and KNO_3. Precipitation of the NO_2^- ion was carried out in each case at a pH of 1.5.

Further, an attempt was made to use the method under discussion for controlling the composition of nitrite baths widely used in our industry for burnishing metals [3]; they usually have the following composition:

NaOH 500-150 g/liter of water
$NaNO_3$ 200-250 g/liter of water
$NaNO_2$ 50-250 g/liter of water.

TABLE 2

Determination of NO_2^- by Means of Nitriton B in Solutions Containing Other Ions; In particular, in Solutions Corresponding in Composition to Baths Used for Burnishing Metals

Series number	NO_2^- taken in mg	Number of analyses	NO_2^- found in mg – $\overline{c}$	$\Sigma (c_i - \overline{c})^2$	s^2	$s_{\overline{c}}$	$t_{0.95} \cdot s_{\overline{c}}$
1	23,0	6	23,03	0,2095	$3,5 \cdot 10^{-2}$	$8,4 \cdot 10^{-2}$	±0,22
2	37,5	6	37,52	$9,21 \cdot 10^{-2}$	$1,5 \cdot 10^{-2}$	$5,5 \cdot 10^{-2}$	0,14
3	34,5	6	34,52	$5,14 \cdot 10^{-2}$	$8,6 \cdot 10^{-3}$	$4,1 \cdot 10^{-2}$	0,11
4	57,5	6	57,49	$6,23 \cdot 10^{-2}$	$1,0 \cdot 10^{-2}$	$4,6 \cdot 10^{-2}$	0,12
5	75,0	6	75,06	0,852	0,14	0,17	0,44

During burnishing, which is carried out at a temperature of 135-150°, alloy components are oxidized and fall as hydroxides into the sludge; in the supernatant electrolyte their concentration is very small. In this connection, the following concentrations were used, 1 liter contained 3.3 g of Na_2SO_4, 0.5 g $NaNO_3$, and $4 \cdot 10^{-4}$ M of $Fe_2(SO_4)_3$, $Cr_2(SO_4)_3$, $NiSO_4$ and $MnSO_4$. These concentrations correspond to a sample from a bath diluted 400 times, while, as special experiments showed, the contents of the heavy metals were considerably higher than those met normally in practice. To 100 ml of such a solution was added a definite amount of $1 \cdot 10^{-2}$ M $NaNO_2$; it was then determined as follows: a saturated sodium carbonate solution was added to precipitate the heavy metals, the precipitates were filtered off and washed with 1% Na_2CO_3; the filtrate was neutralized with 1 M H_2SO_4 using litmus paper as indicator, nitrite was then precipitated by using sufficient Nitriton B, the triazole being determined gravimetrically as described. In all, three series of tests were carried out – Nos. 3-5; the results obtained proved completely satisfactory; they are given in Table. 2.

TABLE 3

Determination of NO_2^- in Cases Where the Triazole is Precipitated by Gradual Acidification of an Alkali Solution Containing Excess Nitriton B

NO_2^- taken in mg	Number of determinations	NO_2^- found $\overline{c}$ in mg	$\Sigma (c_i = \overline{c})^2$	s^2	$s_{\overline{c}}$	$t_{0.95} \cdot s_{\overline{c}}$
35.0	5	38.03	5.71	1.14	0.53	±1.47
25.0	5	27.99	4.44	0.89	0.47	1.31
10.0	6	10.76	3.12	0.52	0.32	0.82

Since, in some instances, there are materials containing the nitrite ion, which give solutions with pH > 7, we checked on the possibility of precipitating the triazole by gradual acidification of such a solution, containing an excess of Nitriton B added beforehand, to a pH of 1.5-2.8. The results obtained which are given in Table 3 show poor reproducibility, since the dispersion s^2 is very high, and, in each case, in the first two series, no doubt includes systematic errors, since the range $c \pm t_{0.95} s_{\overline{c}}$ does not include the true value of the NO_2^- ion concentration.

The results given above enable us to recommend the procedure described above – by means of which the results given in Table 1 were obtained – for the gravimetric determination of nitrite ions using Nitriton B. Apparently, this method can be used in many instances, in particular for determination of NO_2 in pickles used in the food industry [4]; it is especially suitable in this case, since the polarographic method recommended for this purpose gives satisfactory results only when a number of precautions are taken.

SUMMARY

1. A new gravimetric method has been developed for the determination of nitrite ions as benzenesulfanyl-o-phenylenediazimide (atriazole), which is formed by the interaction of NO_2^- with the o-aminoanilide of benzenesulfonic acid (Nitriton B).

2. The properties of Nitriton B have been studied, as well as those of the triazole formed by its interaction with NO_2^- ions; in particular, the solubility of the triazole in water has been determined.

3. Conditions for precipitation have been determined which assure getting best results in the presence of other ions, and an analytical procedure has been worked out.

Received August 19, 1955

LITERATURE CITED

[1] N. P. Komar and I. Yu. Martynchenko, "Trans of the Kharkov State University Chemical Institute, 12, 253 (1954).

[2] N. P. Komar, J. Anal. Chem., 7, 325 (1952) (T. p. 361).*

[3] P. K. Lavorko, "Oxidation of Metals", State Scientific and Tech. Press of Literature on Machine Building, 1952, p. 8.

[4] R. Pletikha and E. Krzhizhova, J. Anal. Chem., 9, 366 (1954) (T. p. 407)*.

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

A MICROFLOTATION METHOD OF ANALYZING HEAVY WATER

I. P. Gragerov

L. V. Pisarzhevsky Institute of Physical Chemistry

For isotopic analysis of water with a low content of heavy isotopes of hydrogen and oxygen, the method most widely used is the flotation method [1], which gives an accuracy of ~1%, but requires not less than 2-3 g of water. Accordingly, several micro methods have been developed, of which the most widely used is the microflotation method proposed in 1933 by Gilfillan and Polanyi [2]. This method consists in measuring the pressure at which a state of flotation is achieved for a float immersed in standard water, this float having an elastic head and a reservoir which is filled through a narrow opening with test water; the density of this water is found from the value of the flotation pressure by means of a calibration curve relating flotation pressure to the density of the water in the float; the curve in turn is drawn by determining the flotation pressure for a float successively filled with several samples of water of known density. A few tenths of a ml of water is required for analysis; its accuracy is 2-3%.

This method has the following essential drawbacks: 1) the elastic properties of the float head change rapidly; this means frequent calibration; 2) the relation between the density of the water with which the float is filled, and flotation pressure is non-linear in character; this complicates calibration; 3) it is difficult to determine flotation pressure sufficiently accurately, since it depends on several parameters; 4) it is necessary to carry out calibration and all analyses at the same temperature, exact establishment of which in thermostats of the usual type is difficult.

In the present article we have described a modification of the Gilfillan and Polanyi method, in which a non-resilient float of the type depicted in Fig. 1 is used, while the state of flotation is achieved as in normal flotation methods, by changing temperature and not pressure. When such modifications are used, the drawbacks enumerated above are eliminated.

For isotopic analysis of water by our method, flotation temperatures T_1 and T_2 are found for the float filled with standard water and with test water respectively, when the float is immersed in each case in standard water. Afterwards, by means of tables for changes of density of water with temperature, we determined the increase in density Δd_{outer} of the water, in which the float is immersed, on changing the temperature from T_1 to T_2. The value of Δd_{outer} is related to the sought for excess density Δd of the test water (as compared with the standard water). This relation is determined as follows. A float of total volume V, partly filled to volume v with water of density d_1, and immersed in water of density D_1, floats at a temperature T_1. In order to achieve a new state of flotation after filling the float with water of different density (d_2), it is necessary to change the temperature to T_2. When this is done, the density of the water outside the float changes to D_2, while the density of the water in the float changes to $d_2 + (D_2 - D_1)$. The new state of flotation is achieved when the change in weight of the float and the water filling it becomes equal to the change in the weight of water displaced by it, i.e. when

$$V[(d_2 + D_2 - D_1) - d_1] = V(D_2 - D_1)$$

or

$$\Delta d = \Delta d_{outer} \cdot \left(\frac{V}{v} - 1\right) = \Delta d \quad K. \qquad (1)$$

The coefficient K* is determined experimentally by determining the value of Δd_{outer} for one sample of water with a given Δd.

It is evident from Equation (1), that the absolute error in determining Δd is equal to the error in determining Δd_{outer}, multiplied by K. When $K < 1$, this error can, in principle, become less than that in the usual flotation method, and becomes smaller, the smaller K**. The use of this ratio for further increasing the accuracy of the flotation method of water analysis is not excluded.

Description of the Method

Construction of Float. The floats which we used (20-30 mm long) are depicted in Fig. 1. It is clear from Equation (1) that the value of coefficient K is smaller, the nearer to unity the value of the ratio V/v. In order to get a favorable value for this ratio, the floats were made with thin walls (but not so thin that they became sensitive to pressure variations). Chemically stable glass capillaries 1.5-2 mm in diameter with a wall thickness of ~ 0.1 mm proved suitable for constructing the floats. The top and bottom parts of the float were made separately with long drawn out pieces as shown in Fig. 2a, and then fused together. An opening of diameter 0.03-0.05 mm was made by rotating in the flame the evenly cut end of the lower part of the float fused to the other end until the opening ceases to be visible. The size of the opening was controlled by measuring with a microscope. The dimensions of the top and bottom part of the float were chosen so that the float, when filled with standard water, floated in the same water, (i.e. in some more standard water) at a temperature 5-6° higher than room temperature. A bit of glass is taken off or put on the float in order to adjust it for the required temperature. A convenient length for the shaft is 50-60 mm (Fig. 2b), so that it can be heated without expulsion of water from the float. The shaft is only given its final shape after completion of adjustments.

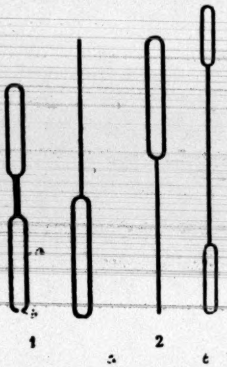


Fig. 1. Floats for micro-flotation analysis of heavy water.
Figs. 2a and 2b. Order in which construction operations were carried out.

Cleaning, Storage, and Handling of the Float. The float is washed with a freshly prepared solution of $KMnO_4$ in concentrated sulfuric acid and carefully rinsed with clean water. Wash liquor will enter on immersing the float warmed in hot water in it*.**. Forceps made from elastic steel wire and with platinum tips, as shown in Fig. 3 are used for handling the float for washing purposes.

Floats are stored as shown in Fig. 4 and are handled by means of the platinum hook also shown in the diagram.

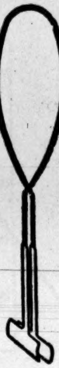
Purification of Water for Analysis. 0.03-0.05 g of water sample is placed in the test tube a of the apparatus shown in Fig. 5, and frozen with liquid air; the apparatus is then evacuated to a pressure of 1-3 mm Hg. Tap b is closed and the water heated to 30-40°, its vapors pass into a quartz tube c, 45 cm long heated to 800°: this tube is filled with cupric oxide; the vapors condense in the cooled tube d which contains a few mg of Ag_2O for neutralization. The water is then driven from tube d into tube e containing the float. Two discs f of sintered glass prevent dust from the air and from cupric oxide from falling into e. Trap g cooled with liquid air holds back any oil vapors from the pump. Thick vacuum grease is put on all the ground glass joints.

---

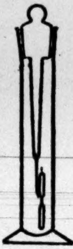
* The ratio V/v, which determines the value of K, does not depend on the temperature despite the fact that the values of V and v depend on temperature.

** Inaccuracy in the value of K does not play a part in determining the excess density of one water sample as compared with another, which usually interests research workers; accordingly, we did not take it into account.

*** We took into account thermal fatigue of the glass by checking, on the day analyses were made, the flotation temperature of the float, filled with standard water; it has no effect on the value of coefficient K.



3



4

Fig. 3. Forceps for manipulating the float.
Fig. 4. Vessel for storing the float.

The purification scheme just described is only suitable for water containing excess deuterium. For heavy oxygen water analysis, cupric oxide and Ag_2O should be omitted, and purification confined to several vacuum distillations. Water containing volatile impurities should be given a preliminary purification.

Filling the Float. Air is led into test tube e after distilling the test, in order to fill the float. When this is done, water enters the evacuated float; usually, however, a small bubble of gas remains; to remove this, tube e is turned upside down, by rotating the apparatus in the ground glass joints. On doing this the float will not drop, since it clings to the wall, while the bubble will float up to the open end. By gentle tapping, the water covering the tip of the float flows out, and the apparatus is rapidly evacuated (better still, tap b is opened and closed a few times, while the pump is operating), by turning the apparatus back to its normal position and letting air in. After one or two such operations, the bubble becomes almost invisible; for its final removal, it is dissolved, by compelling it to move in the water filling the float (by rocking the apparatus). During this operation care should be taken that the end of the float remains in the water all the time. Before transferring the float into the test tube to be used for analysis, in order to prevent penetration of air into it during the transfer, the float is kept for a few minutes in the apparatus while it is cooled with ice.

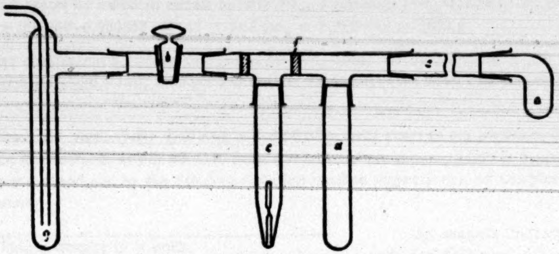


Fig. 5. Apparatus for preparing samples for analysis and for filling the float.

Calibration of the Float and Analytical Procedure. The filled float is washed twice on the outside with distilled water at room temperature (held in the platinum hook) and transferred into the test tube used for analysis, containing the same freshly distilled water. Test tube + water are kept in a thermostat all day when analyses are being carried out, otherwise, water saturated in the cold with air, on heating, will give off bubbles which settle on the float and interfere with work*.

The flotation temperature is determined, as in normal flotation methods, by determining the rates of immersion and emersion of the float at several temperatures near to the flotation temperature, constructing appropriate graphs, and interpolating to zero velocity. The simple and reliable thermostat which we used, was developed long ago in our institute [3], and ensured constancy of temperature within 0.001-0.002°.

---

* Bubbles can be removed by means of the platinum hook.

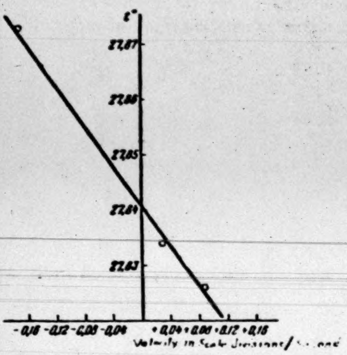


Fig. 6. An example of the graph used for determining flotation temperature.

The following example shows how to find coefficient K and carry out the analysis:

It was found that the float filled with water of normal isotope composition (standard) which was purified in our apparatus, moved upwards with a rate of 0.089 of a scale division in 1 second at 27.826°, with a rate of 0.029 division at 27.834°, and a downward rate of 0.173 division in 1 second at 27.873°.

According to these results, as can be seen from Fig. 6, the flotation temperature works out at 27.841°. The flotation temperature, determined in the same way, for a float filled with water with an excess density of $\Delta d = 1277$[*], proved to be 25.779°.

From tables of density for ordinary water we find Δd_{outer} as a difference in densities at 25.779 and 27.841°; $\Delta d_{outer} = 0.996868 - 0.996305 = 563\ \gamma$. from which:

$$K = \frac{\Delta d}{\Delta d_{outer}} = \frac{1277}{563} = 2.268.$$

After filling the float with water of unknown excess density Δd_x, a flotation temperature of 26.102° was found, from which $\Delta d_{outer} = 0.996782 - 0.996305 = 447\ \gamma$ and $\Delta d_x = 2.268 \cdot 477 = 1082\ \gamma$.

As shown experimentally, coefficient K hardly changes at all with time. On the other hand, the flotation temperature of a float filled with standard water, changes somewhat; accordingly we determined it on the day when analyses were made.

The method described has been successfully used over a period of several years in our institute; it ensures an accuracy of 2% on the value determined, as can be seen from the table where a comparison is made of results obtained by means of our method and by the ordinary flotation method respectively, on samples obtained by diluting water of known density.

Sample number	Excess density in γ units		
	Macromethod	Micromethod	Calculated
1	1069, 1067, 1069	(1068)[**], 1071, 1072	(1068)[**]
2	754, 753	756, 747	757
3	523, 522	519, 525	526
4	259, 258	254, 254	260

An analysis (including purification of the water) takes 1.5-2 hours.

Evacuation of the Float. The float is evacuated by placing it in tube e (Fig. 5) and the apparatus evacuated. After evaporation of all the water, float and apparatus are ready for a new analysis. During systematic analysis, it is sufficient to wash the apparatus and float with sulfuric acid and permanganate once every 5-10 days.

SUMMARY

A new variant of the micro-flotation method has been suggested for the analysis of heavy and heavy-oxygen water, whereby it is possible to analyze 0.03-0.05 g of water with an accuracy of 2% in the course of 1.5-2 hours.

Received December 18, 1954

---

[*] The excess density of water used for calibration can be measured accurately by the usual flotation method or by diluting an aliquot of heavy water of known composition.

[**] Original for calibration and dilution.

LITERATURE CITED

[1] A. I. Brodsky, "Chemistry of Isotopes", Moscow, 1952; K. Kirshenbaum, "Heavy Water," 1953.

[2] G. S. Gilfillan and M. Polanyi, Z. Phys. Chem., 166, 254 (1933).

[3] O. K. Skarre, S. G. Demidenko, and A. I. Brodsky, J. Phys. Chem., 9, 152 (1937).

BLANK
PAGE

SEPARATION OF NIOBIUM, TANTALUM, AND TITANIUM BY EXTRACTION

F. V. Zaikovsky

All-Union Scientific Research Institute of Economic Mineralogy, Moscow

Isolation of niobium, tantalum, and titanium, as well as their separation from other metals of the fourth, fifth, and sixth groups of the Mendeleev Periodic Table which accompany them , is one of the most difficult problems of analytical chemistry.

It is clear from the work of Schoeller, Powell, and Alimarin, et al. [1-6, 17-19], that the use of hydrolysis, and of precipitants such as tannin, salicylic acid, calcium chloride, cinchonine, phenylarsonic acid, and pyrogallol does not lead to a quantitative separation of titanium from elements associated with it.

Wernet's research [7], on the separation of niobium, tantalum, and titanium based on the use of differences in the solubility of their ammonium salts in concentrated hydrochloric acid, did not yield reliable results.

Methods for the separation of small amounts of titanium from niobium and tantalum by chromatographic extraction were recently published [8-10]. The methods have their points, but have some essential drawbacks: they are difficult to carry out technically because of the necessity of carrying out work in half-shaded vessels with complex fluoride complexes of niobium, tantalum, titanium, and other elements, and use up to a liter of methylethyl ketone for one analysis; comparative quantitative results for extent of the separation of titanium from niobium and tantalum are not given.

The difficulties of separating titanium from elements which accompany it (niobium, tantalum, and zirconium) are connected with the fact that they do not give normal true solutions; the chemist has to work with complex fluorides or oxalate and tartrate compounds in aqueous solutions; they are not very reactive and do not readily enter into chemical reactions.

Schoeller [1], reasoned that the difficulties of separating niobium, tantalum, titanium, zirconium, tungsten, and certain other elements are connected with "loss of individual properties".

It is known however [11-13], that the individual properties of niobium, tantalum, and titanium, both when they are present simultaneously, or individually, are clearly manifested with respect to polyfunctional phenols having hydroxyl groups in positions 1, 2 or 1, 2, 3 (pyrogallol, pyrocatechol, etc.). Niobium in weakly alkaline solution, or in a neutral oxalate medium gives, with phenols of this type, complex compounds of a yellow color; tantalum forms similar compounds in acid media, while titanium gives a yellow-orange complex compound in acid or alkaline media.

We made it our aim to separate titanium from niobium and tantalum, by extracting their pyrocatechol complex compounds from an oxalate medium at various pH values.

EXPERIMENTAL

A Study of the Conditions for Extracting the Complex Compound of Titanium and Pyrocatechol

During extraction of the titanium-pyrocatechol complex in oxalate solution by certain organic solvents, the complex imparts a yellow-orange color to them.

The changeover of color from one phase to the other does not necessarily indicate extraction of the element. It was essential to study this point experimentally. To do this a standard solution containing 1 mg/ml of titanium (calculated as TiO_2) was prepared. To 500 mg of TiO_2 in a porcelain crucible was added 6-7 g of potassium pyrosulfate and the whole slowly heated till a clear melt of a yellowish color was obtained. The cooled melt was dissolved in hot 3% ammonium oxalate solution, in an amount sufficient to give 500 ml of solution. To 10 ml of the oxalate solution (10 mg TiO_2) was added 10 ml of 3% ammonium oxalate, and at a pH of 3.0 5 g of pyrocatechol dissolved in it; after 5-6 minutes, the solution was transferred to a 100 ml separating funnel, and extracted with an equal volume of n-butanol saturated with water. The extract was separated from the aqueous phase, and the butanol evaporated in a porcelain beaker on a water bath; the residue obtained was treated with 20 ml of 10% sulfuric acid, and then, after precipitation with cupferron [14, 16], the titanium was determined either gravimetrically or colorimetrically by the peroxide method [15].

In addition to butanol, the organic solvents listed in Table 1 were tested as potential extractants.

It is clear from Table 1, that titanium is only extracted by polar organic solvents; the highest separation coefficient was achieved with butanol; slightly inferior to this was a mixture of chloroform and butanol, while acetylacetone, ethyl acetate, and methyl butyl ketone were still more inferior in that order.

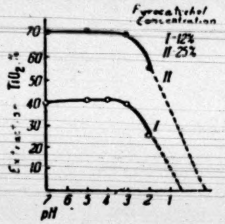


Fig. 1.

It follows therefore from Table 1 that the best extractant for the titanium-pyrocatechol complex is butanol. The distribution coefficient for titanium between the two phases when present in equal amounts, can be increased or decreased by varying experimental conditions, above all by changing the pH of the oxalate solution, and the pyrocatechol concentration respectively (Table 2, Fig. 1).

As is evident from Table 2 and Fig. 1, the optimum conditions for extracting titanium are a pH of the oxalate solution of 7-3, and a pyrocatechol concentration of ~25%; the distribution coefficient of titanium is equal to 2.20-2.40. The distribution coefficient may be increased by increasing the pyrocatechol concentration; when, however, this is done, a homogeneous mass is obtained which it is difficult to separate into phases.

Distribution of titanium between phases when the amount of the phases is varied, is shown in Table 3.

TABLE 1

Distribution of Titanium Between Organic Solvent Phase and Water

Extractant used	Distribution of titanium in %		K*
	in extractant	in water	
Chloroform + n-butanol (1:3)	64.0	36.0	1.78
n-Butanol	70.0	30.0	2.33
Methylsalicylate	0.00	100.0	~
Benzene	0.00	100.0	~
Ethyl ether	0.00	100.0	~
Ligroine	28.0	72.0	~
Methyl butyl ketone	0.00	100.0	0.40
Isoamyl alcohol	31.0	69.0	~
Acetylacetone	24.0	76.0	0.45
Ethyl acetate	0.80	99.2	0.31
Chloroform			0.08

* K – distribution coefficient – ratio of titanium concentration in the extractant to that in the aqueous phase.

It is clear from Table 3 that increasing or decreasing the volume of the extractant – butanol – does not affect the phase distribution of titanium. Titanium is distributed between the phases – organic solvent and water in the ratio 70 : 30. Consequently, increasing extractant volume does not give any positive effect.

It is clear from Table 3, that for extraction, one should take a volume of butanol approximately equal to half the volume of the original oxalate solution (aqueous phase). The titanium-pyrocatechol complex probably has a high solubility in butanol, but some of the titanium is not complexed, and cannot transfer to the butanol phase.

The results given in Table 4 were obtained during a study of the relation between titanium distribution and its concentration in the oxalate solution, for an equal volume of the phases, at a pyrocatechol concentration of 20%, and a pH of 3.0.

TABLE 2

Relation Between Titanium Distribution and pH of the Oxalate Solution, and Pyrocatechol Concentration (Original Concentration 0.5 mg/ml TiO_2)

pH	Pyrocatechol concentration in %	Distribution of titanium in %		K
		Butanol	Aqueous phase	
7	12.0	40.2	59.8	0.68
5	12.0	40.0	60.0	0.67
4	12.0	43.2	56.8	0.76
3	12.0	40.4	59.6	0.68
2	12.0	26.0	73.6	0.36
7	25.0	69.0	31.0	2.23
5	25.0	70.4	30.0	2.33
3	25.0	70.8	29.2	2.42
2	25.0	55.2	44.8	1.232

TABLE 4

Distribution of Titanium Between Butanol and Aqueous Phases in Relation to Titanium Concentration

TiO_2 concentration in mg/ml	Distribution of titanium in %		K
	Butanol	Aqueous phase	
0.500	55.12	44.88	1.228
0.333	57.60	42.40	1.358
0.210	62.58	37.42	1.672
0.125	72.00	28.00	2.571

TABLE 3

Distribution of Titanium Between the Butanol and Aqueous Phases in Relation to the Volumes of the Phases (Pyrocatechol Concentration 25%, pH 3)

TiO_2 concentration in mg/ml	Ratio of phases in ml		Distribution of titanium in %	
	Aqueous phase	Butanol	Butanol	Aqueous phase
1	20	10	70.5	29.5
1	10	10	70.3	29.7
0.5	40	20	70.8	29.2
0.5	20	20	69.2	31.8
0.5	12	20	69.0	31.0

It is evident from Table 4 that on decreasing titanium concentration four times, i.e. from 0.5 to 0.125 mg/ml, the distribution coefficient doubles. During extraction, it is expedient to work with less concentrated titanium solutions.

As a result of experimental work, the following optimum conditions for phase distribution of titanium were found: pH 7-3, concentration of pyrocatechol in the oxalate solution 20-25%, a low titanium concentration in solution, and a volume of butanol equal to half of that of the original oxalate solution.

Properties of Metal Pyrocatechinates

In addition to titanium, the following metals form colored complexes with pyrocatechol: iron (III) and (II), uranium (VI), tantalum (V), niobium (V), molybdenum (VI), tungsten (VI) and vanadium (IV). Results on the extraction of the pyrocatechinates of these metals from an oxalate medium are given in Table 5.

TABLE 5

Extraction of Metal Pyrocatechinates from Oxalate Solutions by Butanol

Metal	Extraction of pyrocatechinate		Color	
	pH 2-5	pH 5-8	pH 2-5	pH 5-8
Iron (III)	–	–	–	Blue-violet
Iron (II)	–	–	–	Blue
Uranium (VI)	–	–	–	Brown
Titanium (IV)	+	+	Yellow-orange	Yellow-orange
Niobium (V)	–	+	–	Yellow
Tantalum (V)	+	+	Yellow	–
Molybdenum (VI)	–	–	Yellow-orange	Red
Tungsten (VI)	–	–	Orange	Yellow-green
Vanadium (V)	oxidized	oxidized	Red	Blue

+ extracted
– not extracted

The elements which accompany niobium and tantalum (zirconium, tin, etc.) are not extracted from an oxalate solution; they do not form colored complexes with pyrocatechol, and do not interfere with phase distribution.

It is clear from Table 5, that at pH 5-8, niobium, tantalum, and titanium are extracted, while at pH 2-5, only tantalum and titanium are extacted. Consequently, on this basis, it is possible to separate titanium, tantalum, and niobium from other elements which do not give colored complexes with pyrocatechol, and also from elements, which, in the form of pyrocatechinates are not extracted by butanol (iron, molybdenum, etc). Moreover, it also follows from Table 5, that titanium and tantalum can be separated from niobium in more acid media (pH 2-5). On the basis of the results given in Table 5, it is possible to map out a method of separating the elements: titanium and tantalum are first separated from niobium by using a very acid oxalate medium; subsequently, titanium and tantalum are separated.

Separation of Titanium and Tantalum

The properties of the titanium- and tantalum-pyrocatechol complexes respectively, differ from each other in oxalate solution: the complex with titanium is not stable in a strongly acid medium, the analogous complex with tantalum is however stable even in a very acid medium. The same is true in butanol solution. Moreover, on treating the extract with acid or alkali solution (Table 5), titanium should be distributed between the aqueous and butanol phases. When this is done, a definite amount of titanium, depending on the given conditions, goes back from the butanol extract during each re-extraction into the aqueous phase.

Re-extraction of titanium from the organic phase increases on using sulfuric acid, and drops off slightly on using hydrochloric acid; other acids proved unsuitable. Distribution of titanium between extract and acid, increases with increasing acidity (Fig. 2).

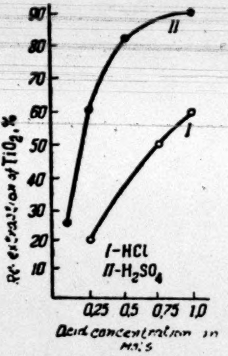


Fig. 2

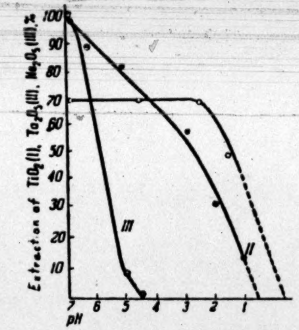


Fig. 3

Neutral, or weakly alkaline solutions proved less suitable: titanium pyrocatechinate (like the corresponding niobium complex) is more stable in neutral or weakly alkaline media and is difficult to re-extract under such conditions.

Experiments were carried out as follows: in 50 ml lots of oxalate solution, containing tantalum and titanium (0.2 mg/ml of each), at differing pH values (from 1 to 7; the pH was established by means of universal indicator) was dissolved 12 g of pyrocatechol. Solutions were quantitatively transferred from the beakers in which they were made to 100 ml separating funnels, and extraction of the pyrocatechinates of titanium and tantalum was carried out with 25 ml lots of butanol saturated beforehand with water.

TABLE 6

Separation of Tantalum and Titanium

TiO_2 taken in mg			Found after separation in mg	
Ta_2O_5	TiO_2	Ta_2O_5	Ta_2O_5	TiO_2
10.00	10.00	1 : 1	10.20	9.8
1.00	10.00	10 : 1	1.08	10.1
0.25	10.00	40 : 1	0.25	9.9
0.50	10.00	20 : 1	0.50	10.1
10.00	10.00	1 : 1	9.90	10.0
5.00	10.00	2 : 1	5.10	10.0
0.20	10.00	50 : 1	0.20	10.1
0.10	10.00	100 : 1	0.08	10.1
1.00	10.00	10 : 1	0.95	9.9
2.00	10.00	5 : 1	2.00	10.0

In order to separate the titanium-pyrocatechol complex, the extract containing tantalum and titanium was treated in a separating funnel a few times with 5% sulfuric acid. During the last extraction, the aqueous phase should be colorless or have a pale-yellow color, which indicates practically complete removal of titanium (aqueous phase) from the tantalum (extract). The extract was evaporated on a water bath and to the residue was added 15-20 ml of water; the whole was then evaporated again almost to dryness; the residue was finally dissolved in 30 ml of 10% sulfuric acid by heating; after cooling, 8-10 ml of cupferron solution was added. The residue was filtered off, transferred to a crucible, dried, calcined, and the residue fused with the least possible amount of potassium pyrosulfate. The cooled melt was dissolved by heating in 25-50 ml of ammonium oxalate. The oxalate solution was adjusted to a pH of 7-8 by means of a sodium sulfate solution, ~ 5% of pyrocatechol dissolved in it, and the whole transferred to a separating funnel; tantalum pyrocatechinate was extracted once with half the volume of solution of butanol. The extract was treated 2-3 times with 5% sulfuric acid, and, as indicated above, the tantalum was transferred into an oxalate solution – 10 ml – (or any other necessary volume); tantalum was then determined colorimetrically by the pyrogallol method, or gravimetrically after precipitation with cupferron [14].

Titanium (after removal from tantalum) was determined gravimetrically by the cupferron method [14, 16].

Experiments showed that ~ 70% of the titanium can be extracted by one treatment at a pH of 3.0-7.0 (Fig. 3, Curve 1), while extraction of tantalum increases with increasing pH of the oxalate solution (Fig. 3, Curve II); at a pH of 7, extraction of tantalum is 100%.

Table 6 gives the results of separation of tantalum and titanium from an oxalate solution (50 ml) under the following conditions: pH 3, concentration of pyrocatechol during repeated extractions – 20%, a volume of butanol half the volume of oxalate solution to be extracted. Four extractions of tantalum and titanium are necessary for quantitative separation. Subsequent procedure was the same as that described above.

It is clear from Table 6, by using the method described, that it is possible to separate these elements quantitatively even for ratios of $TiO_2 : Ta_2C_5$ of 100 : 1. It is particularly difficult to separate traces of titanium (< 100 γ) from tantalum. On repeated extraction at pH 7 however, it is possible to remove even such small amounts as these from tantalum.

Phase Distribution of Niobium with Respect to pH of the Oxalate Solution

Niobium forms a complex with pyrocatechol in neutral or weakly alkaline media (Table 5). At a pyrocatechol concentration of ~ 5%, niobium goes over quantitatively from an oxalate medium into the butanol in the form of a yellow niobium-pyrocatechol complex.

Tests were carried out as follows: to 50 ml of an oxalate solution of niobium (0.2 mg/ml), at pH values ranging from 3 to 7, was added 2.5 g of pyrocatechol. After the latter had dissolved, the solution was transferred to a separating funnel and extracted once with half its volume of butanol. The extract was separated from the aqueous phase, butanol removal by evaporation, and the residue dissolved in 25 ml of dilute sulfuric acid; niobium was finally determined either gravimetrically with cupferron, or colorimetrically by the pyrogallol method [11, 14].

It was established in this way that niobium, as the pyrocatechinate, is transferred quantitatively into butanol at a pH of 7 (Fig. 3, Curve III); it starts to be extracted at a pH of 4.5. It is clear from Fig. 3 that niobium, tantalum, and titanium, have a different phase distribution.

At a pH of 7, 100% of the niobium and tantalum pass over from the aqueous phase into butanol, while only 70% of the titanium passes over, in each case for a pyrocatechol concentration of 25%; on lowering pyrocatechol concentration to 6-12% extraction of titanium drops to 40% (Table 2).

A Method for Separating Niobium, Tantalum, and Titanium

As a result of preliminary work the following analytical procedure was adopted: a mixture of the oxides of niobium, tantalum, and titanium, in amounts of up to 20-22 mg, was fused with ~ 1 g of potassium pyrosulfate; the cooled melt was dissolved by heating in 25-50 ml of 3% ammonium oxalate, and sodium sulfate or dilute sulfuric acid added dropwise to the solution until the pH was 3 (using Tropeoline 00 as indicator): pyrocatechol was then added in an amount equal to ~ 20% of the original solution. The solution was transferred to a separating funnel and repeatedly extracted with half its volume of butanol, pyrocatechol being added each time.

After 4-5 extractions, the oxalate solution became almost colorless, indicating quantitative removal of titanium. The last extraction with butanol was carried out without addition of pyrocatechol. After extractive separation of titanium and tantalum, the oxalate solution, containing niobium, was transferred from the funnel to a flask and a colorimetric or gravimetric determination carried out [11, 14].

TABLE 7

Separation of Niobium, Tantalum, and Titanium

Taken in mg				Found in mg		Error in %	
TiO_2	Nb_2O_5	Ta_2O_5	$\frac{TiO_2}{Me_2O_5}$	Ta_2O_5	Nb_2O_5	Ta_2O_5	Nb_2O_5
10,00	1,00	1,00	5 : 1	0,95	1,08	— 5,0	+ 8,0
10,00	10,00	0,30	1 : 1	0,33	9,60	+10,0	— 4,0
10,00	10,00	0,20	1 : 1	0,20	9,70	0,0	— 3,0
10,00	0,50	0,50	10 : 1	0,50	0,52	0,0	+ 4,0
10,00	5,00	1,00	5 : 3	1,04	4,88	+ 4,0	— 2,5
10,00	10,00	0,50	1 : 1	0,53	9,72	+ 6,0	— 2,8
10,00	15,00	0,25	1 : 1,5	0,30	15,40	—12,0	+ 2,6
20,00	0,40	0,30	30 : 1	0,33	0,44	+10,0	+10,0
20,00	0,20	0,20	50 : 1	0,20	0,20	0,0	0,0
—	5,00	0,10	—	0,09	4,80	—10,0	—4,0
—	10,00	0,10	—	0,00	9,80	—10,0	—4,0

The extract (first two combined extracts), containing tantalum and titanium, was treated in a separating funnel a few times with 5% sulfuric or hydrochloric acid in order to remove the titanium. During the last re-extraction the solution should be colorless or have a weak yellow color, indicating an almost complete removal of titanium (aqueous phase) from tantalum (extract). The extract (after removal of the aqueous phase) was evaporated on a water bath, and to the residue was added 15-20 ml of water and the whole re-evaporated; the residue was dissolved on heating in 20-25 ml of 8-10% sulfuric acid (for quantities of tantalum < 1 mg, 1 mg of a 1% salt solution was added as collector) and after cooling 8-10 ml of 3% cupferron solution. The cupferronates were filtered off, transferred to a crucible, dried, and calcined, and the residue fused with as little as possible of potassium pyrosulfate. The cooled melt was dissolved on heating in 20 ml of 3% ammonium oxalate. After dissolving ~ 5% of pyrocatechol in it, the oxalate solution was adjusted to a pH of 7-8 by means of sodium sulfate, transferred to a separating funnel and the tantalum pyrocatechinate extracted once with 8-10 ml butanol. The extract was treated 2-3 times with 5% sulfuric acid, and then evaporated, and, as indicated above, the tantalum was transferred to an oxalate solution — 10 ml — or the requisite volume, and colorimetric determination of tantalum carried out [11, 14].

Results on the separation of niobium, tantalum, and titanium, are given in Table 7.

It is clear from Table 7 that niobium, tantalum, and titanium can be quantitatively separated with not too great an error of up to ± 10%. It is also possible, again as shown in Table 7, to separate two elements, i.e. niobium and tantalum.

In conclusion we should point out that niobium, tantalum, and titanium form complexes with all polyfunctional phenols having hydroxyl groups in the 1, 2 or 1, 2, 3 positions, but not all the compounds of these elements with the phenols are extracted. It is easier to extract the pyrocatechinates than the pyrogallates. Niobium, tantalum, and titanium cannot be extracted at all in the form of their compounds with protocatechuic aldehyde or protocatechuic acid respectively.

Carboxyl, aldehyde, and sulfonate groups in the phenol molecule prevent solution of the complex in the extractant, though these phenols themselves, containing these same groups, are more readily soluble in water, than e.g. in butanol. The same is true of the analogous derivatives of pyrogallol and alizarine. The high solubility of the reagent-complexing agent in the extractant favors the transfer of the element from the aqueous phase to the organic phase. The reagent-complexing agent goes over from the aqueous phase into the organic phase together with niobium, tantalum, or titanium.

When the properties of the phenol, containing hydrophilic (sulfonate group, carboxylic, etc) groups, are closer to water than to the extractant, and if the complexing agent itself is incapable of going over from the aqueous phase to the organic one, then only the color of the complex can be observed, but not its extraction.

During our work we payed attention to the concentration of the pyrocatechol during extractive distribution of the elements, particularly titanium. At high concentrations of pyrocatechol in oxalate solution (20-25%) the properties of titanium with respect to the aqueous phase are not manifested separately: pyrocatechol is extracted together with titanium, since it is more soluble in butanol than in water. Such phenomena are observed e.g. when calcium, as the stearate, is readily extracted by an organic solvent; while in true solutions of calcium, this process is not observed. The chemical nature of the solvent is of significance. Pyrocatechol is sparingly soluble in chloroform or benzene, and metal pyrocatechinates do not pass over into these extractants.

No relationship was observed between pyrocatechol concentration and tantalum during phase distribution. Even at pyrocatechol concentrations of 0.25%, tantalum quantitatively passed over into butanol from an oxalate solution at a pH of 7.

Tantalum passes over as the pyrocatechinate from the aqueous phase into the organic one at a concentration of 0.5 mg/ml. Niobium, at the same concentration, quantitatively passes into the butanol as the pyrocatechinate at concentrations of pyrocatechol in the oxalate solution of more than 3%. Niobium passes over into the butanol considerably more readily than titanium, but not so readily as tantalum. The changeover into the organic phase, is probably determined by differences in stability of the oxalate complexes. The stability of the oxalate complexes can be arranged as follows: Ti > Nb > Ta. Quantitative transfer of the pyrocatechinates into the organic phase may be arranged in the following order: Ta < Nb < Ti.

During re-extraction the reverse phenomenon is observed: titanium passes into the aqueous phase more readily than tantalum. Only hydrogen fluoride will effect a transfer of tantalum into the aqueous phase.

SUMMARY

1. Niobium, tantalum, and titanium, as the pyrocatechinates, depending on the pH of the oxalate solution, can be extracted with n-butanol.

The phase distribution of the pyrocatechinates of niobium, tantalum, and titanium has been studied under various conditions, and, on this basis, a method is suggested for the quantitative separation of these elements. The method in essence depends on the fact that titanium and tantalum can be separated from niobium at a pH of 3. Titanium and tantalum are separated by re-extraction with 5% sulfuric acid, followed by repeated extraction of the tantalum pyrocatechinate for a low pyrocatechol content. The method gives experimental errors of the order of ± 10%.

2. It has been established that only niobium, tantalum, and titanium can be extracted as their pyrocatechinates, for a definite phase distribution for each element; other elements (iron, zirconium, tin etc.) are not extracted, and do not affect phase distribution.

Received November 22, 1954

LITERATURE CITED

[1] W. P. Schoeller, The Analytical Chemistry of Tantalum and Niobium, London, 1937.

[2] W. P. Schoeller and A. R. Powell, "Analysis of Minerals and Ores Containing Rare Elements", Chem. Tech. Press, Leningrad, 1928.

[3] I. P. Alimarin and B. I. Frid, Factory Lab., 7, Nos. 8-9, 913 (1938).

[4] I. P. Alimarin and B. I. Frid, Factory Lab., 7, No. 10, 1109 (1938).

[5] I. P. Alimarin and B. I. Frid, Trans. All-Union Conference on Analytical Chemistry, Vol. II, 1943, p. 333.

[6] A. Noyes and V. Bray, "Qualitative Analysis of Rare Elements" Gen. Sci. Tech. Press, 1936.

[7] J. Wernet, Z. anorg. Chem., 267, 4-5, 213 (1952).

[8] F. Burstall, et al., J. Chem. Soc., 1947 (1952).

[9] A. F. Williams, J. Chem. Soc., 3155 (1952).

[10] F. Burstall, et al., Analyst, 77, 983 (1952).

[11] N. F. Krivoshlykov and M. S. Platonov, Trans. All-Union Conference on Analytical Chemistry, Vol. II, 1943, p. 359.

[12] Yu. V. Karyakin, and M. P. Telezhnikova, J. Appl. Chem., 19, 4, 435 (1946).

[13] O. Tomicek and L. Jarman, Chem. Listy, 46, 3 (1952).

[14] J. Ikenberry, et al.,, Anal. Chem., 25, 9, 1340 (1953).

[15] E. B. Sandell "Colorimetric Determination of Metal Traces", State Chem. Press, 1949, p. 481.

[16] V. F. Gillenbrand and G. E. Lendell, "Practical Textbook on Inorganic Analysis" Gen. Sci. Tech. Press, 1937, p. 131.

[17] V. A. Oshman, Factory Lab., 12, 2, 254 (1946).

[18] G. W. Milner and A. A. Smales, Analyst, 79, 933, 315 (1954).

[19] G. W. Milner and A. A. Smales, Analyst, 79, 940, 452 (1954).

SEPARATION OF MAGNESIUM, ALUMINUM, CHROMIUM, MANGANESE; IRON NICKEL, AND COPPER BY AN ION-EXCHANGE METHOD

D. I. Ryabchikov and V. F. Osipova

V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow

Numerous investigations have been devoted to the application of ion-exchange chromatography in analytical chemistry for the selective separation of a component which it is desired to determine. The literature on this problem includes review articles symposiums and monographs which have appeared recently [1-8]. In works published earlier [8-13], the advantages of the ion-exchange method over the chemical methods normally empoyed for separation have been demonstrated.

In the present article we have given a number of examples of separation of metals during analysis of alloys, in which the synthetic cation-exchange resin KU-2 was employed.

Separation of Copper from Aluminum. During analysis of bronzes containing aluminum, copper is deposited electrolytically on a mercury cathode. It is simpler to separate these methods by means of a cation-exchange resin.

One of the methods for separating copper and aluminum by means of a cation-exchange resin is based on the capacity of copper to give a complex compound with thiosulfate [14], according to the equation:

$$2CuSO_4 + 6Na_2S_2O_3 \rightarrow 2Na_3[Cu(S_2O_3)_2] + Na_2S_4O_6 + 2Na_2SO_4.$$

On addition of sodium thiosulfate to a solution of copper and aluminum salts, until the solution is decolorized, copper is converted into the complex anion $[Cu(S_2O_3)]^3$, while aluminum remains unchanged as Al^{3+}. The solution treated in this way is passed through a column filled with a cation-exchange resin in the Na-form; the active groups of the resin only hold back aluminum ions. Copper as the complex thiosulfate anion passes through into the filtrate. When this method is used, the cation-exchange resin cannot be employed in the H-form, since acid would be formed in the column which would break down the anion $[Cu(S_2O_3)]^3$, and the copper would also be absorbed by the resin. The filtrate plus washings are acidified with HCl and boiled until the solution is perfectly clear. The precipitate of copper sulfide formed is dissolved and copper determined iodometrically. Aluminum is eluted from the column with 4N HCl. It is determined in the eluate by the hydroquinoline method.

Results for separation of copper from aluminum in synthetic mixtures are given in Table 1.

As is evident from the results, satisfactory separation of copper from aluminum is achieved. Another method of separating copper and aluminum is based on making use of the amphotericity of aluminum, and the formation of ammines. Addition of ammonia to a solution containing copper and aluminum, leads to the formation of the ammine $[Cu(NH_3)_4](NO_3)_2$. Aluminum, however, is precipitated as the hydroxide. On addition of sodium hydroxide to this intensely blue-colored solution + precipitate, the precipitate of $Al(OH)_3$ dissolves to form the aluminate $NaAlO_2$. In the final solution which has been formed as the result of this successive treatment with ammonia and sodium hydroxide respectively, the copper and aluminum are in solution in the form of complex ions of opposite charge: $[Cu(NH_3)_4]^{2+}$ and $[AlO_2]^-$.

TABLE 1

Taken in g		Found, after separation, in g	
Cu	Al	Cu	Al
0.0300	0.0300	0.0305; 0.0295; 0.0290	0.0320; 0.0298; 0.0320
0.0600	0.0100	0.0600; 0.0620; 0.0590	0.0101; 0.0109; 0.0098

The cation-exchange resin must be in the Na-form for separation of these ions. If the resin is used in the H- or ammonium form, then the aluminate, on passing through the column will be converted back into the hydroxide which will be held up between the particles of resin. Aluminum will, accordingly, not be found in the filtrate.

On passing a solution of the salts of copper and aluminum, treated successively with ammonia and alkali, through a column of the resin in the Na-form, copper as the ammine will be absorbed by the active groups of the resin:

$$2RSO_3Na + [Cu(NH_3)_4]^{2+} \rightarrow (RSO_3)_2[Cu(NH_3)_4] + 2Na^+.$$

The aluminate will pass through such a column into the filtrate. The filtrate containing the aluminate, together with wash water is neutralized with acetic acid and aluminum determined as indicated already by the hydroxyquinoline method.

Copper is eluted from the column with 4N HCl. As a result of this treatment, the resin is regenerated:

$$(RSO_3)_2[Cu(NH_3)_4] + 6HCl \rightarrow 2RSO_3H + CuAl_2 + 4NH_4Cl.$$

Copper is determined in the filtrate iodometrically. After removal of copper, the resin will be in the H-form. In order to convert the resin back into the Na-form, a 5% solution of NaOH is passed through the column; the column is finally washed with distilled water to a neutral reaction. Results for separation of copper from aluminum by this method are given in Table 2.

TABLE 2

Taken in g		Found, after separation, in g	
Cu	Al	Cu	Al
0.0300	0.0300	0.0290; 0.0310; 0.0300	0.0290; 0.0300; 0.0310
0.0300	0.0100	0.0320; 0.0300; 0.0290	0.0110; 0.0095; 0.0090
0.0100	0.0300	0.0095; 0.0110; 0.0100	0.0285; 0.0310; 0.0290

Separation of copper from aluminum by this method gives satisfactory results also.

Separation of Copper, Aluminum, and Magnesium. Initially it was suggested that copper, aluminum, and magnesium could be separated on the basis of the interaction of the mixture of salts in solution with ammonia and alkali. In this case however, magnesium will be precipitated as the hydroxide. Dissolving the $Mg(OH)_2$ in the presence of ammonium chloride did not give good results either. On passing such a solution, containing excess ammonium chloride, through a column of cation-exchange resin in the Na-form, aluminum is also precipitated as the hydroxide, as the result of hydrolysis. Accordingly, in order to remove copper, test solution was treated with thiosulfate till it was colorless. On passing such a solution through a column in the Na-form, copper as the ion $[Cu(S_2O_3)_2]^{3-}$ passed through into the filtrate and was determined as usual.

The active groups of the resin, in addition to the aluminum, also absorb magnesium:

$$2RSO_3Na + Mg^{2+} \rightarrow (RSO_3)_2Mg + 2Na^+.$$

To separate the magnesium and aluminum absorbed on the column, use is made of the amphotericity of the latter. In this case a solution of 5% alkali was used for washing the aluminum ions off the column:

$$(RSO_3)_3Al + 4NaOH \rightarrow 3RSO_3Na + Na\,AlO_2 + 2H_2O.$$

Aluminum was determined in the filtrate by the usual method. Alkali washing of the column does not lead to removal of the magnesium held by the active groups of the resin; this can only be affected by washing the column, after alkali treatment, with 4N HCl.

$$(RSO_3)_2Mg + 2HCl \rightarrow 2RSO_3H + MgCl_2.$$

TABLE 3

Ratio • Cu : Al : Mg	Taken in g			Found, after separation, in g		
	Cu	Al	Mg	Cu	Al	Mg
1 : 1 : 1	0,0300	0,0300	0,0300	0,0300; 0,0284; 0,0295	0,0330; 0,0320; 0,0295	0,0300; 0,0310; 0,0300
2 : 1 : 1	0,0600	0,0300	0,0300	0,0620; 0,0620; 0,0600	0,0320; 0,0300; 0,0295	0,0330; 0,0310; 0,0310
1 : 2 : 1	0,0300	0,060	0,0300	0,0290; 0,0280; 0,0320	0,0595; 0,0610; 0,0630	0,0295; 0,0310; 0,0300
1 : 1 : 2	0,0300	0,0300	0,0600	0,0300; 0,0295; 0,0298	0,0277; 0,0279; 0,0300	0,0630; 0,0600; 0,0610
2 : 2 : 1	0,0600	0,0600	0,0300	0,0620; 0,0610; 0,0600	0,0600; 0,0595; 0,0620	0,0320; 0,0300; 0,0310
2 : 1 : 2	0,0600	0,0300	0,0600	0,0600; 0,0620; 0,0600	0,0290; 0,0300; 0,0300	0,0610; 0,0610; 0,0600
1 : 2 : 2	0,0300	0,0600	0,0600	0,0290; 0,0288; 0,0290	0,0578; 0,0600; 0,0579	0,0610; 0,0600; 0,0600

• Satisfactory results were also obtained in this rather more complicated mixture.

TABLE 4

Ratio Fe : Cr	Taken, in g		Found, after separation, in g	
	Fe	Cr	Fe	Cr
1:1	0.0100	0.0100	0.0100	0.0101
2:1	0.0100	0.0050	0.0110	0.0050
1:2	0.0050	0.0100	0.0050	0.0100
4:1	0.0400	0.0100	0.0410	0.0120
1:4	0.0100	0.0400	0.0100	0.0390

Magnesium was determined in the filtrate by the hydroxyquinoline method. Results for the separation of copper, aluminum, and magnesium are given in Table 3.

Separation of Chromium from Iron. For separation of chromium from iron, use was made of the difference in stability of their thiocyanate complexes. On heating a solution of a chromium salt with ammonium thiocyanate, a stable complex is formed.

$$CrCl_3 + 6NH_4SCN \rightarrow (NH_4)_3[Cr(SCN)_6] + 3NH_4Cl.$$

The complex formed between iron and thiocyanate under the same conditions is very unstable.

Passage of the intensely colored solution formed, containing these metals, through a column in the H-form leads to their separation. Chromium as the complex anion with the composition $[Cr(SCN)_6]^{3-}$ readily passes into the filtrate. On heating the filtrate with nitric acid, the complex chromium compound is decomposed; after treatment with sulfuric acid chromium is determined by the persulfate-silver method.

The iron in the solution being analyzed is absorbed by the active groups of the resin:

$$3RSO_3H + Fe^{3+} \rightarrow (RSO_3)_3Fe + 3H^+.$$

After removal of chromium as the complex anion, iron is eluted from the column with 4 N HCl. After washing the column until there is no longer any reaction for iron (thiocyanate test), iron is determined in the second filtrate + washings, by one of the usual methods.

Results for separation of this pair of elements are given in Table 4.

Chromium and iron can also be separated by another method. As indicated above, chromium gives a complex compound with thiocyanate, which is considerably more stable than the iron one. With pyrophosphate, the reverse holds true.

The pyrophosphate complex of iron is formed according to the equation:

$$2FeCl_3 + 3Na_4P_2O_7 \rightarrow Na_6[Fe_2(P_2O_7)_3] + 6NaCl;$$

the complex thus formed, is so stable, that the complex anion $[Fe_2(P_2O_7)_3]^{6-}$ still exists at a pH of 1. It is interesting to note that the anionic form of iron is maintained also at very high pH values of 10-11, when ammonia is added to the original solution. Under these conditions, there is a sharp change in the color of the solution from yellow to red, which is, presumably, connected with a transformation into the inner sphere of the complex according to the reaction:

$$Na_6[Fe_2(P_2O_7)_3] + 4NH_4OH \rightarrow 2Na[FeP_2O_7(NH_3)_2] + Na_4P_2O_7 + 4H_2O.$$

The complex formed between chromium and pyrophosphate breaks down completely at a pH of 3, to form the simple chromium cation.

As a result of experimentally chosen conditions, a mixture of iron and chromium can be separated quite well, if the solution acidified to a pH of 1-3 contains pyrophosphate in amounts no less than in the ratio $Me^{3+} : P_2O_7^{4-} = 1:4$. Test solution prepared in this way will contain the two metals in the form of ions of opposite charge: $[Fe_2(P_2O_7)_3]^{6-}$ and Cr^{3+}. On passing such a solution, containing oppositely charged ions, through a column in the Na-form, iron will pass into the filtrate, while chromium will be held by the active groups of the resin:

$$3RSO_3Na + Cr^{3+} \rightarrow (RSO_3)_3Cr + 3Na^+.$$

Iron is separated from the filtrate by boiling it with alkali and is then determined by one of the usual methods. Removal of chromium from the column is effected by eluting the latter with 10% H_2SO_4:

$$2(RSO_3)_3Cr + 2H_2SO_4 \rightarrow 6RSO_3H + Cr_2(SO_4)_3.$$

Chromium is determined in the second filtrate by the same method. Results for the separation of chromium and iron by the pyrophosphate method are given in Table 5.

These results demonstrate that, in this case, chromium and iron are separated satisfactorily.

TABLE 5

Ratio Fe : Cr	Taken in g		Found, after separation, in g	
	Fe	Cr	Fe	Cr
1 : 1	0,0100; 0,0100		0,0100; 0,0102	0,0103; 0,0101
1 : 2	0,0050; 0,0100		0,0051; 0.0050	0,0100; 0,0101
2 : 1	0,0100; 0,0050		0,0107; 0,0103	0,0050; 0,0053
1 : 10	0,0050; 0,0500		0,0051; 0,0050	0,0511; 0,0515
10 : 1	0,0500; 0,0050		0,0503; 0,0512	0,0052; 0,0050

Separation of Manganese from Iron. Manganese can be readily separated from iron, as in the previous instance, by using sodium pyrophosphate as complexing agent. On acidifying the interacting solutions to a pH of 2-3, only iron forms a complex anion. On passing the solution through a column in the Na-form, manganese under these conditions will be held by the active groups of the resin:

$$2RSO_3H + Mn^{2+} \rightarrow (RSO_3)_2Mn + 2H^+.$$

Iron passes into the filtrate. After breakdown of the complex, iron is determined as usual.

Manganese is washed off the resin with 10% H_2SO_4.

$$(RSO_3)_2Mn + H_2SO_4 \rightarrow 2RSO_3H + MnSO_4.$$

Manganese is determined in the filtrate by one of the usual methods. Results for the separation of iron and manganese are given in Table 6.

Separation of Chromium from Manganese. On the basis that chromium alone forms a complex anion $[Cr(SCN)_6]^{3-}$ with thiocyanate, while manganese remains as the simple cation Mn^{2+}, these two metals can be readily separated from each other by means of a column of resin in the Na-form. The practical procedure for separating this pair of elements is the same as that described for the separation of iron from chromium. Results for the separation of a mixture of manganese and chromium are given in Table 7.

TABLE 6

Taken in g		Found, after separation, in g	
Fe	Mn	Fe	Mn
0.0400	0.0200	0.0381; 0.0410; 0.0327	0.0179; 0.0190; 0.0219

Separation of manganese and chromium is also possible on the basis of formation of a stable complex compound between chromium and pyrophosphate. An oily liquid with a dark green color separates out from a solution of chromium plus pyrophosphate on addition of a mixture of alcohol and ether. On drying in a desiccator over concentrated sulfuric acid, this oily liquid crystallizes. According to analytical results, the composition of the material formed corresponds to the formula: $Na_5[Cr(P_2O_7)_2]H_2O$. Thus, chromium on interacting with pyrophosphate (on heating) in solution appears in the form of a complex anion: $[Cr(P_2O_7)_2]^{5-}$, while manganese under the same conditions, is found in the form of the simple Mn^{2+} cation. On passing a mixture of the ions of these metals through a column filled with a cation-exchange resin in the Na-form, only chromium passes through into the filtrate, while manganese is absorbed by the active groups of the resin. First chromium, and then, after washing off the column, manganese, are determined in the filtrates separately, by the usual methods. Results for separation of manganese and chromium on the basis of a pyrophosphate treatment are given in Table 8.

TABLE 7

Taken in g		Found, after separation, in g	
Mn	Cr	Mn	Cr
0.0100	0.0090	0.0100; 0.0110; 0.0100	0.0093; 0.0098; 0.0089

TABLE 8

Taken in g		Found, after separation, in g	
Mn	Cr	Mn	Cr
0.010	0.0090	0.0120; 0.0130; 0.0100	0.0097; 0.0089; 0.0094
0.010	0.0100	0.0110; 0.0120; 0.0110	0.0090; 0.011 ; 0.010

TABLE 9

Taken in g			Found, after separation, in g		
Fe	Cr	Mn	Fe	Cr	Mn
0.030	0.009	0.010	0.031; 0.031; 0.028	0.0087; 0.0093; 0.0113	0.0133; 0.0131; 0.0149

Separation of Iron, Chromium, and Manganese. On the basis of the reactions described above, separation of mixtures consisting of iron, chromium, and manganese, can be effected by various methods. Possibly, a more effective variant is that in which use is made of the capacity of iron to give a stable complex compound with pyrophosphate at low pH values. In this case, iron, as the negative complex anion $[Fe_2(P_2O_7)_3]^{4-}$, passes into the filtrate, while chromium and manganese (Cr^{3+}, Mn^{2+}) are absorbed by the active groups of the resin. After removal of chromium and manganese from the column, they are separated from each other by converting the chromium into the thiocyanate complex. On repeated passage of the solution through a column in the Na-form, chromium passes into the filtrate as the anion $[Cr(SCN)_6]^{3-}$, in which it is determined. The manganese absorbed by the column is eluted by means of 10% sulfuric acid.

Table 9 contains the results on separation of a mixture consisting of iron, chromium, and manganese.

Separation of Chromium and Nickel. During analysis of steel, separation of this pair of metals by means of ion-exchange chromatography is also simple. In this case again, it is possible to make use of the capacity of chromium to form a stable complex with thiocyanate, while nickel remains as the divalent cation under these conditions. On passing a mixture of the dissolved metals through a column containing a cation-exchange resin in the Na-form, nickel is absorbed by the active groups of the resin:

$$2RSO_3Na + Ni^{2+} \rightarrow (RSO_3)_2Ni + 2Na^+.$$

Chromium passes into the filtrate as $[Cr(SCN)_6]^{3-}$. Nickel is eluted from the column with 4 N HCl. Nickel is determined by one of the usual methods.

Results for the separation of chromium and nickel are given in Table 10.

TABLE 10

Taken in g		Found, after separation, in g	
Cr	Ni	Cr	Ni
0.0500	0.1500	0.0477; 0.0496; 0.0490	0.1462; 0.1510; 0.1490

Examples are given below of the chromatographic separation of metals in production samples.

1. Determination of Chromium. 0.05 g of ferro-chrome is dissolved in 30 ml of H_2SO_4 (1:2) by heating on a sand bath. 5 ml of HNO_3 is added and the mixture heated till white fumes of sulfuric acid appear. Metals are precipitated by ammonia as hydroxides; the precipitates are filtered off and dissolved in hydrochloric acid. The solution of chlorides is evaporated to dryness, the dry residue is dissolved in water, and, after addition of 10 ml of 5% NH_4SCN, the whole is evaporated to dryness again. The final residue is dissolved in a small amount of water, and the solution passed through a column in which the resin (20 g) is in the H-form; the column is washed with distilled water.

Filtrate plus wash water containing the thiocyanate complex of chromium is used for the quantitative determination of chromium. Iron is not determined quantitatively. To the filtrate containing chromium 1-2 ml of HNO_3 is added to destroy the complex. 20 ml of H_2SO_4 is added to the solution which is then evaporated to the appearance of sulfuric fumes, after which chromium is determined by the persulfate-silver method. In our sample we found 59.60, 59.30, and 59.45% Cr.

Using the same method, chromium was determined in a standard sample N 167, containing 74.60% Ni and 21.1% Cr. In this alloy we found 20.99, 21.38 and 21.18% Cr.

2. Determination of Iron. 0.1 g of ferro-manganese is dissolved in 50 ml of HCl by warming, 1-2 ml of hydrogen peroxide is added to the solution to oxidize divalent iron; it is then evaporated to dryness and the dry residue dissolved in 15-20 ml of water. 25 ml of 10% sodium pyrophosphate (pH 3) is added to convert iron into the complex anionic form. The solution obtained is passed through a column with a cation-exchange resin in the Na-form. NaOH is added to the filtrate plus wash liquor and the whole boiled for destroying the iron pyrophosphate complex. Ferric hydroxide is filtered off and after repeated reprecipitation, the iron determined gravimetrically. In our test sample we found 34.63, 35.00, and 34.56% Fe.

SUMMARY

By applying ion exchange chromatographic methods it is possible to separate various metals from their mixtures, with their subsequent determination, more easily than by other methods.

Copper can be separated from aluminum by converting these elements into ions of different charge. On interaction with thiosulfate, only copper forms a complex anion $[Cu(S_2O_3)_2]^{3-}$; while in ammoniacal media, these metals are transformed respectively into various types of complex ions: $[Cu(NH_3)_4]^{2+}$ and $[AlO_2]^{-}$. This technique can be used for separating mixtures of copper, aluminum, and magnesium. In this case, after removal of copper and aluminum as complex anions, magnesium, which remains on the resin in the column, is determined by the usual method after desorption with acid.

Separation of chromium from iron is possible on the basis that in the presence of thiocyanates, only chromium forms a stable complex anion $[Cr(SCN)_6]^{3-}$; iron remains as the simple cation and is absorbed by the active groups of the resin. During interaction of these metals with pyrophosphates, the opposite is true. In this case, iron forms a complex anion $[Fe_2(P_2O_7)_3]^{6-}$; chromium remains as the simple cation.

The reaction with pyrophosphate can also be used for separating iron from manganese. Reaction with thiocyanate is more convenient for separating chromium from manganese. Using the techniques described, it is also possible to separate chromium from nickel, and to separate ternary and quaternary mixtures of the metals listed above.

Received May 31, 1955

LITERATURE CITED

[1] D. I. Ryabchikov and E. A. Terentyeva, Progr. Chem. 19, 2 (1950).

[2] "Chromatography", Collection of Articles, Foreign Lit. Press, 1949.

[3] "The Chromatographic Method of Separating Ions" Collection of Articles, Foreign Lit. Press, 1949.

[4] I. E. Apeltsin, V. A. Klyachko, Yu. Yu. Lurye, and A. S. Smirnov, "Ion-Exchange Resins and Their Application", State Press of Literature on Standardization, 1949.

[5] "Ion Exchange", Collection of Articles, Foreign Lit. Press, 1951.

[6] R. Kunin and R. Myers, "Ion-Exchange Resins" Foreign Lit. Press, 1952.

[7] F. M. Shemyakin, E. S. Mitselovsky, and D. V. Romanov, "Chromatographic Analysis", Chem. Press 1955.

[8] Trans. Commission on Anal. Chem. Vol., 6 (9), 1955.

[9] D. I. Ryabchikov, Trans. Conference on Chromatography, Acad. Sci. Press 1952; J. Anal. Chem., 7, No. 1 (1952) (T. p. 35)*.

[10] D. I. Ryabchikov and A. I. Lazarev, Proc. Acad. Sci., 92, No. 4 (1953).

[11] D. I. Ryabchikov and V. F. Osipova, Proc. Acad. Sci., 96, No. 4 (1954).

[12] D. I. Ryabchikov and M. M. Senyavin, J. Anal. Chem., 8, 195 (1953) (T. p. 215)*.

[13] D. I. Ryabchikov and V. S. Bukhtiarov, J. Anal. Chem., 7, 6 (1952); (T. p. 377)*; 9, 4 (1954) (T. p. 217)*; Factory Lab., No. 1 (1952).

[14] D. I. Ryabchikov and V. G. Silnichenko, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 1, 1947.

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

ÇOLORIMETRIC DETERMINATION OF TRACES OF COPPER IN METALLIC NICKEL AND ITS COMPOUNDS IN THE ULTRA-VIOLET

K. P. Stolyarov and F. B. Agrest

A. A. Zhdanov Leningrad State University

At present, despite the large number of methods for the colorimetric determination of copper [1], there is no satisfactory method for determining traces of copper in nickel, its alloys, and salts. In most methods it is essential to carry out a preliminary separation of copper from elements accompanying it, in particular from nickel and cobalt.

In order to solve this problem, we made use of the capacity of univalent copper to give a complex compound with ammonia, which has a high absorption coefficient in the ultra-violet. The analogous compound of nickel exhibits only a weak absorption in this region. Copper was reduced with ascorbic acid in the presence of potassium bromide. The work was carried out on an ultra-violet photometer [2]. Quartz cuvettes of 3 and 2.5 cm thickness were used.

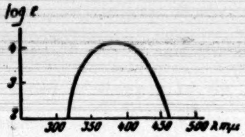


Fig. 1. Absorption curve for the ammonia-bromide complex of copper.
mea

In order to decide at which wave length, colorimetric measurements should be carried out, the character of the absorption of ultra-violet light by the ammonia complex of univalent copper in the wave length range 450 to 300 mμ was studied on a Russian SF-11 spectrophotometer. The absorption curve shown in Fig. 1 was obtained. It is clear from this curve, that the optimum wave length range at which colorimetric measurements can be carried out is that extending from 360-400 mμ.

TABLE 1

Introduced		Cu : Ni	Found	Error	Introduced		Cu : Ni	Found	Error
Cu γ/ml	Ni γ/ml		Cu γ/ml	γ/ml	Cu γ/ml	Ni γ/ml		Cu γ/ml	γ/ml
0,55	800	1 : 1455	0,55	0,00	2,21	1000	1 : 453	2,30	+0,09
0,55	1050	1 : 1910	0.50	-0,05	2,21	1550	1 : 701	2,10	-0,11
0,92	50	1 : 54	0,90	-0.02	3,70	1000	1 : 270	3,70	0,00
0,92	500	1 : 543	0,90	-0,02	3,70	1550	1 ; 419	3,60	-0,10
0,92	1050	1 : 1143	0,92	0,00	11,07	1050	1 : 95	11,10	+0,03
1,48	1000	1 : 676	1,45	-0,03	11,07	1550	1 : 140	11,15	+0,08
1,48	1500	1 : 1014	1,70	+0,22					

Experiments carried out in order to study the stability of the ammonia complex, showed that the highest optical density corresponding to maximum absorption by the complex, is observed on adding 25 ml of ammonia solution (1 : 1) to the test solution. The "color" of the complex attains its maximum density after 30 minutes, and does not change in the course of 20 minutes.

Construction of a Calibration Curve

After choosing the conditions for carrying out colorimetric measurements, we carried out tests to find out whether or not solutions containing the ammonia complex of univalent copper obey Beer's law, and constructed a calibration curve.

In view of the fact that the working solution of the mixture of reagents exhibits light absorption, colorimetric measurements were carried out with respect to a reference solution; to this solution was added 2 ml of a 1% solution of ascorbic acid, 2 ml of a saturated solution of potassium bromide, and 25 ml of ammonia solution (1 : 1), and the total volume made up to 50 ml with distilled water. Optical densities were measured 30 minutes after addition of ammonia.

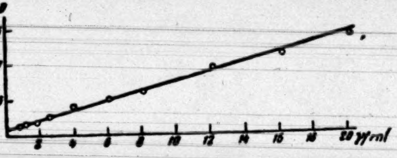


Fig. 2. Calibration Curve.

The shape of the curve, obtained by measurements of a series of solutions containing traces of copper, is shown in Fig. 2. It is evident from this curve that in the concentration range for copper of 0.5 γ/ml to 20 γ/ml a straight line proportionality can be observed between copper concentration and optical density of solution. Within this concentration range therefore, it is possible to carry out colorimetric determination of copper by measuring the absorption of its ammonia complex in the wave-length range λ = 365-380 mμ.

Determination of Copper in the Presence of Large Amounts of Nickel

To determine copper in the presence of nickel we prepared synthetic solution containing small amounts of copper and large amounts of nickel. The amount of copper was determined by means of the calibration curve constructed previously.

As pointed out, the ammonia complex of nickel also exhibits absorption of the ultra-violet in the region 360-380 λ, but this absorption is insignificant. Nevertheless, in order to inhibit this effect of nickel, a similar amount of nickel was added to the reference solution to that contained in test solutions. Using such a technique, nickel does not interfere with copper determination, as can be seen from the results obtained (Table 1), for ratios of Cu : Ni = 1 : 1500.

As can be seen from the results obtained, experimental error for ratios of Cu : Ni ranging from 1 : 1500 to 1 : 100, on an average does not exceed ±3-5%. For ratios greater than 1 : 1500, the error increases sharply, reaching ±10-20%. Moreover, on addition of nickel to solution in amounts greater than 1.55 mg, it starts to be precipitated as $[Ni(NH_3)_6]Br_2$.

It is therefore possible to determine copper with satisfactory accuracy in amounts of 0.05% in nickel.

Determination of Copper in the Presence of Elements Which Accompany It

Apart from copper, metallic nickel and its compounds also contains other metals as impurities (zinc, cobalt, and iron). It was essential to establish the effect of these elements on copper determination. Initially, we carried out tests on solutions containing copper, zinc, and cobalt, but not containing nickel. From the results obtained which are given in Tables 2 and 3, it is clear that cobalt can be present in amounts up to 35 γ/ml, and zinc up to 150 γ/ml.

TABLE 2

Introduced γ/ml		Found	Error
Cu	Co	Cu γ/ml	γ/ml
2,21	1,95	2,20	−0,01
2,21	35,10	2,20	−0,01
2,21	39,00	2 00	−0,21
2,21	54,60	1,20	−1,01
7,36	25,35	7,35	−0,01
7,36	35,10	7,25	−0,11
7,36	39,00	6,50	−1,14
7,36	44,85	6,00	−1,36

TABLE 3

Introduced γ/ml		Found	Error
Cu	Zn	Cu γ/ml	γ/ml
0,92	20,00	0,90	−0,02
0,92	30,10	0,95	+0,03
0,92	100,30	0,96	+0,04
0,92	150,50	1,10	+0,19
0,92	200,70	1,40	+0,48
0,92	401,30	2,00	+1,08
7,36	100,30	7,40	+0,04
7,36	150,50	7,50	+0,14
7,36	200,70	8,10	+0,74

TABLE 4

Introduced γ/ml			Found	Error
Cu	Ni	Co	Cu γ/ml	γ/ml
2,21	643,26	1,95	2,20	−0,01
2,21	643,26	29,26	2,20	−0,01
2,21	643,26	39,00	2,00	−0,21
7,36	643,26	29,26	7,35	−0,01
7,36	643,26	35,10	7,20	−0,16
7,36	643,26	39,00	6,00	−1,36

TABLE 5

Introduced γ/ml			Found	Error
Cu	Ni	Zn	Cu γ/ml	γ/ml
2,21	643,26	50,20	2,20	−0,01
2,21	643,26	150,50	2,25	+0,04
2,21	643,26	200,70	2,50	+0,29
7,36	643,26	50,20	7,35	−0,01
7,36	643,26	150,50	7,60	+0,14
7,36	643,26	200,70	8,90	+1,54

When large amounts of nickel and cobalt were simultaneously present in solution, good results were obtained, similar to those obtained previously (see Tables 1 and 2), as can be seen from Table 4.

As can be seen from Table 4, in the presence of large amounts of cobalt, the optical density of the solution decreases appreciably. This can be explained by the formation of a more stable complex (instability constant $K = 6 \cdot 10^{-36}$) than the corresponding complexes of nickel and copper; this complex does not absorb in the wavelength region $\lambda = 365\text{-}380$ mμ.

Similar experiments were carried out on solutions containing large amounts of nickel and zinc simultaneously. Results are given in Table 5.

As can be seen, in this case, zinc can be present in amounts up to 150 γ/ml. Thus, the presence of such impurities as cobalt and zinc as well as copper, has practically no effect on copper determination in nickel. Nickel and its compounds usually contain iron, which strongly distorts results of copper determinations. Attempts to complex all the iron, or to reduce it to the ferrous state, did not give positive results. Reduction proceeds quantitatively, but the ammonia complex of ferrous iron immediately formed, exhibits strong absorption in the region $\lambda = 365\text{-}380$ mμ.

After a number of tests it was established that iron can be completely co-precipitated with partially precipitated nickel hydroxide. When this is done, as our experiments showed, copper may also be co-precipitated. To avoid this, we reduced copper beforehand to the cuprous state. In this state, copper stays in solution. In this case, experimental procedure was as follows: in a 50 ml beaker was placed a known amount of solution with a given content of copper and nickel respectively; to this was added 2 ml of 1% ascorbic acid solution, and 2 ml of a saturated potassium bromide solution; this mixture was brought to the boil and hydroxides precipitated with ammonia (1:5). Solution plus precipitate was heated for a further 2-3 minutes and the whole rapidly filtered through a small filter into a 50 ml standard flask. The precipitate on the filter was washed with a small amount of hot distilled water. The reference solution was treated in exactly the same way. To the filtrate was added up to 25 ml of ammonia (1:1), and, after 30 minutes, optical densities were measured. The results obtained are adduced in Table 6.

TABLE 6

Introduced in γ/ml			Found	Error	Introduced in γ/ml			Found	Error
Cu	Ni	Fe	Cu γ/ml	γ/ml	Cu	Ni	Fe	Cu γ/ml	γ/ml
2,00	2844,0	—	1,90	—0,10	2,00	2275,2	20,50	2,00	0,00
2,00	3233,2	—	2,00	0,00	2,00	2275,2	68,30	1,90	—0,10
2,00	3792,0	—	2,10	+0,10	6,78	2275,2	13,66	6,80	+0,02
2,00	5193,0	—	1,90	—0,10	6,78	2275,2	40,98	6,75	—0,03
6,78	5193,0	—	6,70	—0,08	6,78	2275,2	80,88	6,85	+0,07
0,68	3994,6	—	0,70	+0,02	6,78	2275,2	101,10	6,60	—0,18
0,68	5193,0	—	0,60	—0,08					

TABLE 7

Introduced in γ/ml					Found	Error
Cu	Zn	Co	Fe	Ni	Cu γ/ml	γ/ml
0,68	50,17	9,25	27,32	2137,76	0,70	+0,02
2,03	100,34	19,50	50,54	2137,76	1,95	—0,08
2,03	50,17	9,75	27,32	4008,30	2,00	—0,03
2,03	75,93	19,50	50,54	4008,30	2,15	+0,12
6,78	100,34	19,50	50,54	2137,76	6,90	+0,12
6,78	50,17	9,75	27,32	4008,30	6,75	—0,03

TABLE 8

Weight of nickel sample in mg	Cu found in mg	Corres-ponding to % cu	% Cu according to spectrographic results
150	0,0200	0,013	
200	0,0325	0,016	0,01—0,03
250	0,0450	0,018	

TABLE 9

Weight of Ni in mg	Cu added in mg	Amount found in mg	Difference in mg	% Cu
200	0,100	0,135	0,035	0,017
200	0,200	0,230	0,030	0,015
250	0,100	0,140	0,040	0,015
250	0,200	0,238	0,038	0,015

It is clear from Table 6 that practically all the iron is co-precipitated with partially precipitated nickel hydroxide. In addition, by using this technique, it is possible to improve the limiting ratios of copper to nickel appreciably; this is particularly important if the nickel contains less than 0.05% of copper. As can be seen from Table 6, for a ratio of Cu : Ni = 1 : 3300, by resorting to co-precipitation, it is possible to determine copper with a very insignificant error (< 3%). Subsequently, experiments were carried out on synthetic solutions containing all the accompanying elements. Results are given in Table 7.

These results show that traces of copper can be determined quite satisfactorily in nickel and its compounds by this technique.

Analysis of Metallic Nickel Samples

In order to check this method for the colorimetric determination of traces of copper in nickel, which we developed by using synthetic solutions, we proceeded to carry out copper determinations in a sample of nickel, in which 0.01-0.03% of Cu had been found by spectrographic analysis; the sample also contained a few hundredths of a percent of zinc; a few thousandths percent of Co, Fe, Al and Si, and ten-thousandths percent of Pb.

Analytical Procedure. An aliquot of nickel was dissolved in dilute nitric acid and the solution obtained transferred to a porcelain basin; a few ml of concentrated sulfuric acid was added and the whole carefully evaporated to dryness. The sulfates obtained were dissolved in a small amount of hot distilled water, and filtered through a small filter into a 50 ml beaker. The filter was washed with hot distilled water, and wash liquor added to filtrate; 2 ml of a 1% solution of ascorbic acid, 2 ml of a saturated potassium bromide solution were then added, and the whole heated to the boil when the hydroxides were precipitated by addition of a small amount of ammonia (1:5). After precipitation heating was continued for a further 2-3 minutes and the solution filtered free of precipitate into a 50 ml standard flask. 25 ml of ammonia (1:1) was added and the volume made up to 50 ml with distilled water; after 30 minutes, the solution was placed in a photometer cuvette, and optical density measured.

Exactly the same amount of nickel as that contained in the test sample was added to the reference solution; subsequently, 2 ml of 1% ascorbic acid solution and 2 ml of saturated potassium bromide solution were added and the whole heated to the boil when precipitation of hydroxides was effected by adding exactly the same amount of ammonia (1:5), as was used in the case of the test sample. After heating, the precipitate was filtered, 25 ml of ammonia (1:1) was added, and the total volume made up to 50 ml. The results obtained are given in Table 8.

In order to check the accuracy of the determination, a known amount of copper was added to the test solution, and the copper contained in the metallic nickel determined colorimetrically by difference. Results are given in Table 9.

From the results given in Table 9, it is clear that they are in good agreement. Analysis may be carried out without evaporating the acid solution to dryness. Nevertheless, in this case, the hydroxides cannot be precipitated with ammonia, since part of it will go to neutralize the free acid, and thereby form a mixture of ammonia and ammonium salts which will hinder precipitation of hydroxides from solution. It is best therefore to precipitate with sodium or potassium hydroxide. Analytical procedure after separation of the hydroxides is the same as in the first instance. The results obtained were no worse; the difficulty when this technique is used, is accurate neutralization of acid solution.

SUMMARY

1. A method has been developed for the colorimetric determination of traces of copper in metallic nickel and its compounds in the ultra-violet region of the spectra; it is based on the absorption of rays of λ = 365-380 mμ by the ammonia complex of univalent copper. The sensitivity of the method amounts to 0.5 γ / ml of copper for a cell thickness of 2.5 cm.

2. Absorption by the ammonia-bromide complex of copper in the visible and ultra-violet over the wavelength range λ = 450-300 mμ has been studied, and an absorption curve for this complex drawn.

3. It has been shown that determination of traces of copper can be carried out for ratios of accompanying elements of Cu : Ni : Co : Zn = 1 : 1500 : 30 : 75 without preliminary separation; by precipitation of traces of iron with part of the nickel as hydroxide, it is possible to increase ratios of Cu : Ni at which copper can still be determined to 1:4,000. A method has been worked out for keeping copper in solution during precipitation of iron and nickel.

4. The method has been checked on a sample of metallic nickel. Analytical procedure is described.

Received July 18, 1954

LITERATURE CITED

[1] A. T. Shoshin and V. N. Ransky, Factory Lab., 8, 1954 (1939); A. A. Tikhonova, Factory Lab., 11, 616 (1945); E. Ya. Yakovleva, Factory Lab., 6, 740 (1951); T. Gallan and I. Henderson, Analyst 54, 650 (1929); H. Moseley, A. Rohwer and C. Moore, Science 79, 507 (1934); E. Laget, Ann. chim. [3] 17, 145 (1935); G. Vastagh, Pharm. Zentrallhalle D., 80, 273 (1939); F. Nydahl, Z. anal. Chem., 116, 315 (1939); M. Golubeva, Hygiene and Sanitation 11, No. 5, 29 (1946); K. Kimura and V. Murakami, Mikrochem. 36/37, 958 (1951); S. V. Svyatsillo and V. M. Luskina, Factory Lab., 9, 1087 (1952); V. A. Generozov, Factory Lab., 20, 45 (1954); G. Spacu and J. Dick, Z. anal. Chem., 71, 79 (1927); A. F. Koblyansky, J. Appl. Chem., 7, 1081 (1934); N. S. Poluetkov and I. Ya. Soloveichik, Dietetic Questions No. 5, 35 (1934); Yu. Yu. Lurye and L. B. Ginsburg, Factory Lab., 3, 271 (1939); A. A. Vasilev and N. P. Vorobeva, Factory Lab., 3, 269 (1939); S. S. Korol, Soil Cultivation No. 3, 126 (1940); I. B. Supunovich and A. B. Konovalova, Factory Lab., 14, 1061, (1948); V. T. Chuiko, Factory Lab., 2, 145 (1951); A. Zh. Shakhkeldyan, J. Appl. Chem., 2, (1929); A. Emmeril, Chem. Weekblad, 27, 552 (1930); S. O. Sinyakova,

J. Appl. Chem., 10, 2109 (1937); N. V. Fedorova, Polygraphic Production No. 8-9, 41 (1938); L. A. Gulyaeva and E. S. Itkina, J. Appl. Chem., 17, 252 (1944); L. M. Kulberg and F. Lirtsman, J. Appl. Chem., 6, 1251 (1936); V. M. Kopeliovich, Factory Lab., 5, 475 (1945); G. I. Aisenberg and E. M. Menshikova, Factory Lab., 12, 673 (1948); V. M. Peshkova, M. E. Levontin and K. I. Litvin, J. Anal. Chem., 3, 161 (1948); M. Ya. Shapiro, Biokhimiya, 13, 323 (1948); M. Ya. Shapiro, Factory Lab., 17, 363 (1951); I. F. Shik, Bulletin of the Mendeleev Chemical Soc., 4, 35 (1940); K. Nance, Anal. Chem., 23,, 1031 (1951); J. Gillis, J. Hoste and E. Caldas, Anales real soc. espan. fis. y quim., B47, 327 (1951); F. Smith, and D. Wilkins, Anal. Chem., 25, 510 (1953); V. T. Chuiko, J. Appl. Chem., 9, 1898 (1936); S. A. Tskhetmel and T. V. Arefeva, Factory Lab., 12, 38 (1946); I. B. Misetskaya, J. Appl. Chem., 19, 400 (1946); I. A. Korshunov and L. N. Sazanova, Factory Lab., 13, 569 (1947); I. A. Korshunov and L. N. Sasanova, Factory Lab., 14, 621 (1948); A. G. Otralberg and R. V. Dityatkovskaya, Factory Lab., 14, 919 (1948); L. M. Kulberg, Factory Lab., 9, 940 (1940).

[2] K. P. Stolyarov and I. A. Stolyarova, J. Anal. Chem., 8, 33 (1953) (T. p. 35)*.

---

* T. p. = C. B. Translation pagination.

RAPID METHODS OF MICRO-ELEMENTAL ANALYSIS

PART 12.* SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN, SILICON, AND HALIDES

V. A. Klimova and E. G. Bereznitskaya

Determination of halogens in halogen-containing organosilicon compounds is carried out independently of C, H, and Si, or simultaneously with Si. Methods for halogen determination differ according to whether halogen in the compound is directly connected to silicon or is found in the organic radical [1-4]. In the first instance, the material is usually first hydrolyzed and then the halogen is determined gravimetrically or volumetrically. Nevertheless, such determinations can be troublesome if there are two halogen atoms connected with the silicon, and even more so when there are three halogen atoms involved. The polymerized siloxanes formed in such cases evelops hitherto undecomposed material and prevents quantitative hydrolysis. Dissolving the compound in ether or alcohol beforehand does not always help one to get better results.

In cases where the halogen is not connected to silicon but to carbon, one cannot just resort to simple hydrolysis; more profound decomposition is required here; usually this is carried out by fusing the material in a nickel bomb with sodium peroxide [5, 6]. When this melt has been dissolved, it is possible to determine halogen and silicon simultaneously; this is the advantage of this particular method. In addition, since fusion is carried out in a bomb, it is possible to analyze volatile compounds. All the same, the large amount of reagents (in comparison with the amount of test sample) which has to be used for fusion will introduce errors as a result of the large amount of salts in the solution of melt, and insufficient purity of the reagents used.

With such compounds, if one only wants to determine halogen, good results can be obtained by means of Korshun and Chumachenko's method [7] – by fusing the material in a steel bomb with metallic potassium.

Determination of carbon and hydrogen in halogen-containing organosilicon compounds is carried out by classical methods, but the results obtained are often unsatisfactory. Usually therefore, research workers confine themselves to determining halogen alone.

Thus, at present, there is no method available which is fairly simple and reliable for the determination of the elements in halogen-containing organosilicon compounds. Another difficulty the analyst comes up against when dealing with these compounds is the extreme instability of some of them with respect to water. In such cases, the possibility of carrying out a simultaneous determination of all the elements, or, at least a few of them, on one aliquot assumes particular importance, since such a determination would allow one to confine oneself to a small amount of test material. The present article is devoted to simultaneous determination of the elements – carbon, hydrogen, silicon, and halogen. In a previous article we described a method for simultaneous determination of carbon, hydrogen, and silicon, in compounds not containing halogens [8, 9]. Combustion of the material is carried out by the rapid method in the presence of chromic oxide on asbestos as catalyst. The catalyst is placed directly in the vessel used for decomposition. Carbon and hydrogen are determined as usual, while the silicon is calculated from the weight of silicon dioxide which is formed in the decomposition vessel. This article is a logical development of this method, and also of the method of Korshun and Sheveleva [10], for simultaneous determination of carbon, hydrogen, and halogen by rapid combustion. In this method, halogen is trapped by silver at 550° in a special apparatus outside the combustion tube, and is determined from the increase in weight of the silver. A platinum contact is placed in the combustion tube, for without it, results for carbon determination are low.

Halogen-containing organosilicon compounds, as our experiments showed, exhibit their own characteristic thermal decomposition under the conditions of rapid combustion; accordingly, simple combination of the methods described above is out of the question.

---

* For Part 11, see J. Anal. Chem. 6, 358 (1955) (C. B. translation p. 347).

Thermal decomposition of halogen-containing organosilicon compounds in the absence of oxidizing agents, and of sufficient oxygen – the state of affairs which holds when combustion is carried out by the rapid method – differs from one class of compounds to the other. Thus, compounds containing C, H, Si, and Cl, and in which the halogen is connected to carbon, and not to silicon, burn without formation of silicon carbide, and results for all four elements are satisfactory, even without addition of oxidizing agent. The halogen which is split off during thermal decomposition, apparently, itself plays the part of an oxidizing agent, and prevents carbide formation.

Decomposition takes a different path when the organosilicon compound contains halogen connected to silicon. In these cases during decomposition, silicon tetrahalide is formed; in addition, in some cases, carbide formation also occurs. The silicon tetrahalide may be carried out of the combustion vessel and absorbed by the silver; as a result determination of both silicon and halide becomes impossible (Table 1). Nevertheless, if the molecule contains enough hydrogen – as our experiments showed, not less than 3% – then the water which is formed during combustion will decompose the silicon tetrahalide to give SiO_2 and the corresponding hydrogen halide, and its formation will not interfere with the determination. Materials which contain less hydrogen than that indicated above can often be analyzed by adding a small amount of water (3-5 mg) to the test aliquot (Table 2). In such cases however decomposition of the compound by water may precede thermal decomposition of the molecule. As a result of interaction with water, the chlorosilane will change over into polymerized siloxanes, and the thermal decomposition of the latter, as Rochow has already pointed out, is usually accompanied by formation of silicon carbide; consequently, combustion of these compounds can only be carried out in the presence of oxidizing agents or catalysts. Accordingly we had to clarify the possibility of carrying out the analysis in the presence of a catalyst which we had adopted, viz. chromic oxide on asbestos *.

Chromic oxide is known to react with chlorine at high temperatures [11]. It may be postulated therefore, that the catalyst which we have used before – chromic oxide on asbestos – may react with the halogen of an organic compound during the thermal decomposition of the latter. Actually, when combustion of hexachloroethane is carried out in the presence of the catalyst Cr_2O_3 on asbestos, we observed the formation of dark brown drops which settle out on the cold parts of the combustion tube. The weight of beaker plus catalyst decreased by 100-500 μg, while no such brown vapors were formed when halogen-containing organic compounds which also contain hydrogen were decomposed under these same conditions, or when samples of hydrogen chloride were evaporated; in these cases the weight of the beaker changed inappreciably. This can apparently be explained by the hydrolyzing effect of water on the halogen compounds of chromium formed (Table 3).

The results obtained show that analysis of halogen-containing organosilicon compounds should be carried out differently, according to the structure of the test compound, and also permit one to develop a method for simultaneous determination of carbon, hydrogen, silicon, and halogen in the various classes of these compounds.

Analysis of Organosilicon Compounds in Which Halogen is Linked to Carbon

Test sample is weighed out into a quartz beaker 70-80 mm long and 4-5 mm diameter, or into a glass ampoule, if the material is volatile. 100-200 mg of asbestos calcined at 1200° is introduced into this beaker and the whole reweighed. When an ampoule is used, it is placed in a beaker with asbestos, with its open end on the bottom of the beaker, so that all the ampoule is inside the beaker. If the ampoule was weighed sealed, then the tip can be broken on the bottom of the beaker.

Beaker plus sample are placed in the combustion tube which contains a contact made from platinum foil. Three absorbent trains are then connected up: the first to be connected up is made of high melting glass or quartz; it is filled with metallic silver and is heated in a special oven to 500-550°; the next in order, is a train for water adsorption; finally the apparatus for absorbing carbon dioxide. In this case, when nitrogen is present in the test material, an absorbent vessel for nitrogen oxides is connected between the last two absorbent vessels. Combustion is then commenced. When combustion is complete the three absorbent vessels and beaker used for combustion are weighed. Silicon is calculated from the increase in weight of the beaker as a result of formation of silicon dioxide; halogen from the increase in weight of the silver; and carbon and hydrogen, as usual (Table 4).

---

* Since polymerized siloxanes are not volatile, a thin layer of chromic oxide on asbestos is sufficient for their complete oxidation.

TABLE 1

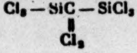
Material	% Halogen		% Silicon		% C		% H	
	Found	Calcu-lated	Found	Calcu-lated	Found	Calcu-lated	Found	Calcu-lated
Bis-(trichlorosilyl) dichloromethane  $Cl_3-SiC-SiCl_3$ ‖ Cl_2	108,80 104,50	80,63	0,57 None	15,96	3,59 3,41	3,41	None 0,13	None
Bis-(trichlorosilyl)-chloromethane $Cl_3SiCHClSiCl_3$	81,92 102,17	78,20	Traces None	17,71	3,78 3,87	3,77	0,78 0,28	0,32

TABLE 2

Material	% Halogen		% Silicon		% C		% H	
	Found	Calcu-lated	Found	Calcu-lated	Found	Calcu-lated	Found	Calcu-lated
Bis-(trichlorosilyl) dichloromethane	80,39 80,26	80,65	16,05 16,37	15,96	3,68 3,47	3,41	None) None	None
Bis-(trichlorosilyl) chloromethane	78,05 78,53	78,20	17,67 17,76	17,68	3,77 3,56	3,79	0,39 0,28	0,32

TABLE 3

Material	Sample weight in mg	Change in weight of beaker in mg	% Halogen		% H		% C	
			Found	Calcu-lated	Found	Calcu-lated	Found	Calcu-lated
Naphthalene	8,92 10,01	— 20 — 30	— —	— —	6,26 6,33	— 6,29	93,80 93,84	93,71
Hexachloroethane . . .	10,53 8,27 10,26 8,23	—560 —200 —110 — 90	83,95 86,94 91,62 90,42	89,87	—	—	10,13 10,23 10,08 10,12	10,12
$C_{13}H_{17}ClO_4$	10,52 10,68	— 60 — 30	12,36 12,76	13,00	6,23 6,34	6,23	57,23 57,32	57,27
Hydrochloric acid	17,65 18,73 20,13 19,24	— 10 — 0 — 10 + 20	—	—	—	—	—	--

Analysis of Compounds in Which Halogen is Connected to Silicon

The majority of compounds of this type can be analyzed by the method described above (Table 5). Materials which contain less than 3% hydrogen are exceptions to this. When compounds of this type are analyzed a drop or two of water (3-5 mg) is added to the beaker containing the test material plus asbestos, and the whole re-weighed. During final calculations, the weight of water added is subtracted from the weight found. For the rest, the analytical procedure is the same as usual (Table 6).

TABLE 4

Material	Found C %	Calculated C %	Difference C %	Found H %	Calculated H %	Difference H %	Found Si %	Calculated Si %	Difference Si %	% Halogen Found	% Halogen Calculated	Difference in % Halogen
Dimethylchloromethylethylsilane	44,04	43,93	+0,11	10,04	9,58	+0,46	20,21	20,55	—0,34	25,98	25,94	+0,04
	44,52	—	+0,59	9,78	—	+0,20	20,16	—	—0,39	26,13	—	+0,19
Trimethyl- γ-chloropropylsilane	47,76	47,81	—0,05	9,88	10.03	—0,05	18,83	18,63	+0,20	23,50	23,52	—0,02
	47,96	—	+0,15	10,02	—	—0,01	18,51	—	—0,12	23,40	—	—0,12
Methyliodomethyldipropylsilane	35,80	35,56	+0,24	7,01	7,09	—0,08	10,47	10,39	+0,02	47,31	46,96	+0,35
	35,72	—	+0,16	7,08	—	—0,01	10,41	—	+0,02	46,63	—	—0,33
1,2-Bis-trimethylsilyl-1,2-dibromoethane	28,94	28,91	+0,03	6,14	6,07	+0,07	16,38	16,91	—0,53	48,18	48,11	+0,07
	28,96	—	+0,05	6,08	—	+0,01	16,28	—	—0,63	48,15	—	+0,04

TABLE 5

Material	Found C %	Calculated C %	ΔC %	Found H %	Calculated H %	ΔH %	Found Si %	Calculated Si %	ΔSi %	Found Cl %	Calculated Cl %	ΔCl %
Dimethylbutylchlorosilane	47,88	47,81	+0,07	10,00	10,03	—0,03	18,94	18,64	+0,30	23,27	23,52	—0,25
	47,77	—	—0,04	10,00	—	—0,03	18,84	—	+0,20	23,03	—	—0,49
Methylnaphthyldichlorosilane	54,51	54,77	—0,16	4,27	4,18	+0,09	11,92	11,65	+0,24	29,10	29,40	—0,30
	54,96	—	+0,19	4,22	—	+0,04	11,78	—	+0,13	29,70	—	+0,30
Propyldichlorosilane	25,32	25,18	+0,14	5,54	5,63	—0,09	20,07	19,63	+0,44	49,11	49,56	—0,45
	25,08	—	—0,10	5,68	—	+0,05	19,64	—	+0,01	49,61	—	+0,05
n-Butyl (β-chlorethyl) dichlorosilane	32,98	32,81	+0,17	6,02	5,97	+0,05	12,33	12,79	—0,46	48,43	48,43	0,00
	33,08	—	+0,22	6,03	—	+0,06	12,91	—	+0,12	48,67	—	+0,24
Phenyl-α-cyanoisopropoxydi-chlorosilane	46,41	46,16	+0,25	4,46	4,26	+0,20	10,87	10,80	+0,07	27,08	27,25	—0,17
	46,49	—	+0,33	4,49	—	+0,23	10,75	—	—0,05	27,00	—	—0,25

TABLE 6

Material	Found C %	Calculated C %	ΔC %	Found H %	Calculated H %	ΔH %	Found Si %	Calculated Si %	ΔSi %	Found Si %	Calculated Si %	ΔSi %
Bis-(trichlorosilyl)dichloromethane	3,68	3,41	+0,27	Нет	Нет	—	16,05	15,97	+0,08	80,39	80,61	−0,22
	3,47	—	+0,06	»	»	—	16,37	—	+0,40	80,26	—	−0,35
Bis-(trichlorosilyl)chloromethane	3,77	3,78	−0,01	0,39	0,32	+0,07	17,67	17,70	−0,03	78,05	78,20	−0,15
	3,56	—	−0,22	0,28	—	−0,04	17,76	—	+0,06	78,53	—	+0,33
1,2-Bis-(trichlorosilyl) chloroethane	7,17	7,25	−0,08	1,01	0,91	+0,10	16,87	16,95	−0,08	75,30	74,89	+0,41
	7,21	—	−0,04	0,96	—	+0,05	16,92	—	−0,03	75,64	—	+0,75
β-chloroethoxytrichlorosilane	11,37	11,23	+0,14	1,98	1,89	+0,09	13,14	13,11	+0,03	65,57	66,29	−0,72
	11,41	—	+0,18	2,02	—	+0,13	13,10	—	−0,01	65,62	—	−0,67

TABLE 7

Material	Found C %	Calculated C %	ΔC %	Found H %	Calculated H %	ΔH %	Found Si %	Calculated Si %	ΔSi %	Found Cl %	Calculated Cl %	ΔCl %
1- Trichlorosilyl-1- dichlorosilylethane	9,34	9,15	+0,19	1,69	1,92	−0,23	21,34	21,40	−0,07	67,94	67,53	+0,41
	9,31	—	+0,16	1,67	—	−0,25	21,19	—	−0,21	68,21	—	+0,68
1, 4-bis-(trichlorosily) butane	15,10	14,78	+0,32	2,38	2,48	−0,10	17,46	17,29	+0,17	65,62	65,45	+0,17
	14,91	—	+0,13	2,29	—	−0,19	16,79	—	−0,50	65,12	—	−0,33
α-Methylisobutylchlorosilane	23,13	23,14	−0,01	4,43	4,37	+0,06	13,50	13,52	−0,02	50,65	51,24	−0,59
	22,99	—	−0,15	4,58	—	+0,21	13,50	—	−0,02	51,02	—	−0,22
Diethylisobutylchlorosilane	47,55	47,81	−0,26	10,04	10,03	+0,01	19,39	18,64	−0,25	23,50	23,52	−0,02
	47,52	—	−0,29	9,95	—	−0,08	18,09	—	−0,55	23,32	—	−0,20
Chlorobutyltyltrichlorosilane	21,14	21,44	−0,30	2,36	2,71	−0,35	12,36	12,54	−0,18	62,97	63,34	−0,34
	21,44	—	0,00	2,58	—	−0,13	12,43	—	−0,11	63,45	—	+0,04
Propyldichlorosilane	25,32	25,18	+0,14	5,54	5,63	−0,09	20,07	19,63	+0,34	49,11	49,56	−0,45
	25,08	—	−0,10	5,68	—	+0,05	19,64	—	+0,01	49,61	—	+0,05

Formation of silicon carbide was observed during attempts to analyze some compounds by the usual method. Silicon carbide was most often formed during analysis of compounds containing three atoms of halogen on one silicon atom, and during analysis of materials which have both hydrogen and halogen on the silicon atom. Such compounds are the most difficult from an analytical point of view, since their combustion cannot be carried out in the absence of chromic oxide. Nevertheless, as already pointed out, in the presence of water, chromic oxide does not interact or hardly interacts at all with halogen, while the small amount of the halogen compound of chromium formed is completely broken down by the water under the experimental conditions. When such compounds are to be analyzed therefore, the following procedure should be adopted.

To the aliquot of test material is added a small amount of chromic oxide on asbestos, a layer of asbestos is then laid down and the whole weighed. A drop of water is placed on the asbestos and the whole re-weighed. Combustion is then carried out as usual. When calculations are made of the water content on the basis of the increase in weight of the apparatus used for absorbing water, the weight of water added at the beginning is subtracted. By means of this method we succeeded in determining the four elements in compounds for which we could not get satisfactory results by means of other methods (Table 7)*.

SUMMARY

1. Decomposition of halogen-containing organosilicon compounds under the conditions used for rapid combustion has been studied.

2. A method has been worked out for the simultaneous determination of carbon, hydrogen, silicon, and halogen in various organosilicon compounds. The accuracy of the method for carbon and hydrogen is ±0.3%, for silicon ± 0.4%, and for halogen ± 0.5-0.6%.

Received July 18, 1955

LITERATURE CITED

[1] Hyde and Delong, J. Am. Chem. Soc., 63, 1194 (1941).

[2] E. G. Rochow, An Introduction to the Chemistry of the Silicones, New York, 1946, p. 162.

[3] D. Gibbons and A. Sykes, Mikrochemie. ver Mikrochim. Acta 40, 76 (1952).

[4] C. Tseng and T. Chao, J. Am. Chem. Soc., 66, 842 (1944).

[5] W. F. Gilliam and H. A. Liebhaftzky, J. Am. Chem. Soc., 63, 801 (1941).

[6] B. A. Fiekers and E. M. Geronimo, J. Am. Chem. Soc., 70, 1654 (1948).

[7] M. O. Korshun and M. N. Chumachenko, Proc. Acad. Sci. USSR, 99, No. 5, 769 (1954).

[8] V. A. Klimova, M. O. Korshun, and E. G. Bereznitskaya, Proc. Acad. Sci., USSR, 96, No. 1, 81 (1954).

[9] V. A. Klimova, M. O. Korshun, and E. G. Bereznitskaya, J. Anal. Chem., 11, 223 (1956) (T. p. 225)**.

[10] M. O. Korshun and N. S. Sheveleva, Proc. Acad. Sci. USSR, 60, No. 1, 63 (1948).

[11] A. Lacourt, Mikrochemie, 23, 308 (1938).

---

* Most of the compounds which are listed in the article were kindly given to us by Corresponding Member A. D. Petrov and his coworkers.

** T. p. = C. B. Translation pagination.

ISOLATION AND SEPARATION OF A MIXTURE OF FORMALDEHYDE AND ACETALDEHYDE BY MEANS OF DIMEDONE

A. F. Lukovnikov

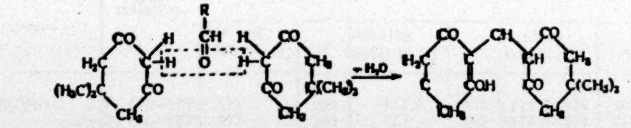
USSR Academy of Sciences Institute of Chemical Physics, Moscow

Isolation and identification of individual compounds from complex organic mixtures is extremely important in studies on the mechanism of chemical reactions. This is of special importance when labeled atoms are used for studying the mechanism. In such cases the reliability of isotopic analysis depends on the chemical purity of the product isolated and on the conditions used for isolating it; under these conditions the possibility of isotopic dilution of the product should be excluded.

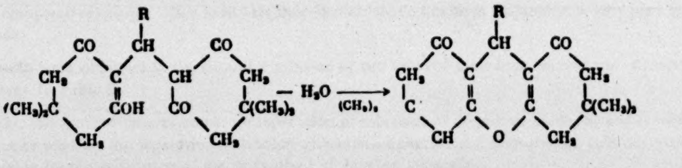
During studies of the reaction mechanism of the oxidation of carbohydrates, considerable attention is given to the study of the part played by aldehydes, the mechanism of their formation, their behavior, etc. Accordingly, research workers used various techniques and methods for quantitative determination and identification of aldehydes.

The most convenient method for identifying aldehydes is to make use of the specific group of the reagent dimedone (5,5-dimethylcyclohexane-dione-1,3 [1]).

On reacting with aldehydes, dimedone forms enol compounds:



On heating the enol derivatives with dilute mineral acids, acetic acid, acetic anhydride, or absolute alcohol, ring closure occurs with separation of water and formation of so called "anhydrides":



Formaldehyde is an exception to this rule; it only forms the enol compounds; the "anhydride" can only be prepared by prolonged heating of the enol with concentrated acids.

Both groups of aldehyde-dimedone derivatives are crystalline compounds with characteristic melting points.

In working with aldehydes, labeled with radio-carbon, the dimedone derivatives are very convenient products, since they are relatively easily isolated from complex organic mixtures, and it is fairly easy to prepare good samples from them for measurement of radioactivity. In addition, it is possible to separate the pure formaldehyde derivative from a mixture of the derivatives of different aldehydes. We have already pointed out that formaldehyde, in contrast to other aldehydes, only forms the enol, which is readily soluble in weak alkali solutions. This property is used for separating the formaldehyde product from the derivatives of the higher aldehydes.

As a consequence of the slight solubility of dimedone in water, precipitation of mixtures of formaldehyde and acetaldehyde is carried out from aqueous-alcohol solutions in the presence of mineral acid. The products isolated are washed with water and dilute alcohol to remove sulfuric acid and dimedone, and then treated with an alkali solution. The enol product of formaldehyde dissolves in the alkali, while the "anhydride" of acetaldehyde remains in the precipitate. The formaldehyde derivative is removed and the solution acidified until weakly acid. This method of separation permits one to get very pure products in a fairly good yield.

In order to separate formaldehyde and acetaldehyde formed during oxidation of hydrocarbons, we carried out a series of tests to check on the completness of the separation of the derivatives of formaldehyde from acetaldehyde, using acetaldehyde labeled with radio-carbon.

The mixture of formaldehyde and labeled acetaldehyde was treated in a 50% alcoholic solution with dimedone in the presence of sulfuric acid. After isolation of the derivatives of formaldehyde and acetaldehyde, they were washed and recrystallized from 50% alcohol. Melting points as well as the specific activity (α impulses/min-mg) of the compounds were then determined. Results of these experiments are given in Table 1.

TABLE 1

Checking on Completness of Separation of CH_2O from CH_3CHO

Compound	After isolation	I Recrystallization		II Recrystallization		III Recrystallization	
		Melting Point in °C	■	Melting Point in °C	■	Melting Point in °C	■
CH_3CHO . . .	1. 171—173°	173	100	173,5	102	173,5—174	102
	2. 171—173°	173	200	173	205	173,5—174	205
CH_2O	1. 186—187°	187,5—8	0	188,5	0	188,5—189,5	0
	2. 186—187°	187,5—8	0	188	0	189	0

As the results in Table 1 show, formaldehyde is completely inactive when the specific activity of the acetaldehyde is comparatively high. This indicates that formaldehyde has been isolated in a very pure state from acetaldehyde.

Similar results were obtained in the case of a mixture of two labeled dimedone derivatives. Results of these tests are given in Table 2.

Accordingly, this method ensures complete separation of mixtures of dimedone products, and it would appear that it can be used for the separation of labeled aldehydes; nevertheless, tests showed that this method is not really applicable for the separation of the derivatives of labeled aldehydes.

We precipitated the same preparation of labeled acetaldehyde from an aqueous-alcohol solution with dimedone in the presence of H_2SO_4 as described above, and also from an aqueous solution with 2,4-dinitrophenylhydrazine in the presence of HCl. After isolation of the dimedonate and the hydrazone, their specific activities were determined. In addition another aliquot of the same acetaldehyde $C^{14}H_3CHO$, was subjected to combustion to give CO_2 and the specific activity of the $BaCO_3$ formed measured. Results are given in Table 3.

TABLE 2

Separation of the Mixture of Labeled Dimedonates of CH_2O and CH_3CHO

Compound	Specific activity in impulses $minutes^{-1} \cdot mg^{-1}$			
	Original products	After separation		
		I Recrystallization	II Recrystallization	III Recrystallization
CH_3CHO	195	194	195	195
CH_2O	72	71	72	72

TABLE 3

Determination of the Specific Activity of CH_3CHO by Various Methods

Compound measured	Specific activity in impulses $minutes^{-1}$, g^{-1}	
	Compound	On one atom of standard compounds
1. Dimedonate isolated from alcoholic solution	120	175
2. Hydrazone	167	191
3. $BaCO_3$	97	194
4. Dimedonate isolated from aqueous solution	132	192

The last column in Table 3 contains the values of the specific activity referred to a standard compound ($BaCO_3$), and related to one labeled atom of acetaldehyde. This calculation was based on the formula

$$\alpha_{\substack{\text{atom}\\ BaCO_3}} = \alpha_{\text{compound}} \frac{M_{\text{compound}}}{197.4}$$

where M_{compound} is the molecular weight of the compound being measured (the dimedone derivative or hydrazone), while 197.4 is the molecular weight of $BaCO_3$.

It is clear from this table that the specific activity of acetaldehyde calculated on the basis of the standard compound in the case of measurements on the dimedone derivative isolated from alcoholic solution, differs considerably from the specific activity found by measurements carried out on hydrazone and $BaCO_3$.

Replicate experiments showed that the specific activity of the dimedonate is 10-20% lower than the values which the hydrazone and carbonate give.

It was found that the drop in specific activity of the dimedonate when derivatives are made in alcohol or alcoholic mixtures may be the result of the fact that the alcohol itself contains aldehyde. In fact, polarographic analysis of the alcohol showed that acetaldehyde was present, its concentration varying in a fairly wide range (up to 4-6 mM/liter).

The alcohol was freed from aldehydes by treating it with 2,4-dinitrophenylhydrazine. When alcohol so treated was used, the specific activity of the dimedone derivative increased somewhat; nevertheless, its activity still remained lower than that of the hydrazone and $BaCO_3$.

This is probably connected with oxidation of C_2H_5OH to CH_3CHO on heating with H_2SO_4 in the air; possibly isotopic exchange occurs between alcohol and aldehyde, or it may be for some other reasons. Obviously, the dimedonate method can only be used if factors which lead to isotopic dilution of acetaldehyde are excluded.

Naturally, we ceased to prepare dimedonates in alcoholic solutions. We therefore prepared them in aqueous solution. Dimedone is only sparingly soluble in cold water (10-15 mg in 100 ml at 20°); nevertheless, in the presence of acids and on heating, its solubility increases. At 100°, upwards of 5 g dissolves in 100 ml water.

Using the enhanced solubility of dimedone in water on heating, we treated the aldehydes (or their mixtures) first, with an aqueous solution of dimedone saturated with the latter at 20°, then crystalline dimedone (2 g for 50 ml) was added, followed by concentrated H_2SO_4 (5 ml for 50 ml of solution); the whole was then heated to the boil in a flask fitted with a reflux condenser and boiling continued for 3-4 hours. Under these conditions, the derivatives of the aldehydes crystallize out immediately in the form of solid compounds which float on top of the liquid. In view of the fact that unreacted dimedone is precipitated on cooling the mixes with the dimedonates, we isolated the precipitate directly from hot solution. When filtration is carried out on a filter funnel specially adapted for filtering hot, or on a porous filter with suction, it is possible to crystallize out only an insignificant amount of dimedonate. Dimedone readily dissolves in slightly warm alkali solutions. This enabled us to separate the acetaldehyde derivative from the derivative of formaldehyde and dimedone. Separation of the formaldehyde derivative from dimedone was carried out after isolating the solid precipitate by washing the latter with 50% alcohol solution. Determination of the specific activity of the acetaldehyde dimedonate separated by such a technique, showed good agreement with results obtained by other methods (see Table 3).

A check on the cleanness of separation of CH_2O and CH_3CHO gave similar results to those described above. Special experiments with marked formaldehyde dimedonate showed complete separation of dimedone from its derivative on treating it with 50% alcohol and recrystallization.

The method described can be applied for isolating and separating mixtures of formaldehyde and acetaldehyde. The pure formaldehyde derivative can be isolated in yields of up to 90%, while that of acetaldehyde can be isolated in yields up to 70%. Obviously, the formaldehyde derivative partially dissolves in alcoholic solution during the process of freeing it from dimedone, while acetaldehyde volatilizes to a considerable extent from the aqueous solution during boiling of the reaction mixture in the preparation of the dimedonates.

It should be pointed out that this method could be successfully used for isolation and separation of derivatives of formaldehyde and acetaldehyde even in cases where their mixture contains up to 20% of other higher aldehydes. Special experiments showed that from a mixture containing 20% of the dimedone derivative of propionaldehyde, the dimedonate of acetaldehyde could be isolated perfectly pure by 3-4 crystallizations from 50% alcohol.

Received May 26, 1955

LITERATURE CITED

[1] V. S. Johnson, R. D. Shennan and R. A. Reed, "Organic Reagents for Organic Analysis", Moscow, Foreign Lit. Press, 1948.

APPLICATION OF β-HYDROXYNAPHTHOIC ALDEHYDE IN ANALYTICAL CHEMISTRY

PART 2. A NEW SEMI-MICRO GRAVIMETRIC METHOD FOR THE DETERMINATION OF COPPER

S. I. Gusev and V. I. Kumov

Molotov Medical Institute

In a previous communication [1], we demonstrated the possibility of determining magnesium quantitatively by means of β-hydroxynaphthoic aldehyde.

Under certain conditions, in ammoniacal, or, in certain cases, in alkaline solutions, this reagent gives sparingly soluble complex compounds with many (except cadmium) divalent metals such as: Cu^{2+}, Be^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Pd^{2+}. The characteristic crystals formed are suitable for the qualitative determination of divalent cations (work along these lines continues).

In the work described in the present article we aimed at studying the conditions of formation of the inner complex copper compound of β-hydroxynaphthoic aldehyde, to study its physico-chemical properties, and to establish the optimum conditions for carrying out quantitative determination of copper in various objects by means of it.

EXPERIMENTAL

Preparation of the Copper Complex of β-Hydroxynaphthoic Aldehyde

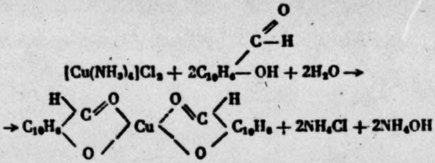
To 100 ml of a $CuCl_2$ solution (containing 0.1 M salt) was added 50 ml of ethyl alcohol and 10 ml of 25% ammonia solution. The mixture was heated to the boil, after which 200 ml of a molar alcoholic solution of β-hydroxynaphthoic aldehyde was added. Immediately, or after a short time interval, a greenish-grey crystalline precipitate of the copper complex of β-hydroxynaphthoic aldehyde was formed. This material was crystallized three times from acetoacetic ester. Analysis of the compound formed gave the following results.

Found %: Cu 15.60; 15.90; C 64.52; 64.85; H 3.45; 3.55.

On the basis of the assumed formula $C_{22}H_{14}O_4Cu$, the following figures were obtained (%): Cu 15.66; C 65.09; H 3.48.

Analysis of the compound for nitrogen gave negative results. The same compound was prepared by the interaction of cupric chloride, pyridine, and β-hydroxynaphthoic aldehyde. Found 64.75% C; 3.54% H.

Formation of the copper complex of β-hydroxynaphthoic aldehyde can be represented by the following scheme:


[Cu(NH₃)₄]Cl₂ + 2C₁₀H₆—OH + 2H₂O →
→ C₁₀H₆ Cu C₁₀H₆ + 2NH₄Cl + 2NH₄OH

Some of the properties of this copper compound are given in Table 1.

TABLE 1

Properties of the Copper Complex of β-Hydroxynaphthoic Aldehyde

Color	Grey-green
Solubility in water (15°)	0.002%
Solubility in alcohol (15°)	0.004%
Solubility in ether (15°)	0.022%
Heating in a capillary in air	At 170°, the compound becomes red brown in color, at 248° it decomposes and is converted into a dark brown mass
Behavior to dilute acids	Does not change in 2 N H_2SO_4
Behavior to dilute alkalis	Does not change in 2 N NaOH
Crystal form under the microscope, see diagram below	

Crystals of the complex compound of copper with β-hydroxynaphthoic aldehyde (× 120).

Quantitative Determination of Copper with β-Hydroxynaphthoic Aldehyde

Gravimetric determination of copper by means of β-hydroxynaphthoic aldehyde was first tried out on pure salts. A standard copper solution was prepared by dissolving 1 g of electrolytic copper in a small amount of nitric acid, the solution was carefully diluted and then made up to 1000 ml with water; the final solution then contained 1 mg Cu/ml. To a copper-ammonia solution heated to the boil was added a 2% alcoholic solution of β-hydroxynaphthoic aldehyde, using 1.5-2 ml of the reagent solution per ml of copper solution. The test solution should contain 50% alcohol. A greenish-grey precipitate separated out, filtered after 25-30 min. through a No. 2 or No. 3 glass crucible, washed 3 times with water and dried to constant weight at 115-120°. The conversion factor to Cu^{2+} is 0.1566. Results are given in Table 2.

It is clear from this table that determination of copper by the method described gives fully satisfactory results. The gravimetric method was further checked on alloys containing other metals apart from copper.

Analysis of Brass (59.0% Cu, 39.5% Zn, 1.5% Pb)

0.1 g of alloys was dissolved in concentrated nitric acid by gradual addition of the latter; to the solution obtained was added ammonia; when an insoluble residue was obtained, this was filtered off, carefully washed with water and the filtrate made up to a 100 ml in a standard flask. To 5 ml of the solution thus obtained was added ~ 3 ml of 95% ethyl alcohol and 1 ml of 25% ammonia; the mixture was heated to the boil, and ~ 6 ml of a heated 2% alcoholic solution of β-hydroxynaphthoic aldehyde was added. After 2-3 minutes a crystalline

TABLE 2

Cu taken in mg	Weight of preciptate in g	Cu found in mg	Absolute error in mg
2	0,0126	1,97	—0,03
2	0,0128	2	—
2,5	0,0160	2,5	—
3	0,0182	2,85	—0,15
3,5	0,0216	3,38	—0,12
4	0,0252	3,95	—0,05
4	0,0252	3,95	—0,05

TABLE 3

Volume of test solution in ml	Weight of precipitate in g	Cu found		
		In mg	In %	By electrolysis in %
5	0,0188	2,94	58,8	59
5	0,0188	2,94	58,8	—
10	0,0372	5,83	58,3	—

precipitate settled out. After 25-30 minutes this precipitate was transferred to a No 2 glass crucible, washed 3 times with water and dried at 115-120°. When 10 ml of test solution was taken, the volumes of the reagents indicated were correspondingly increased. Results for determination of copper in brass are given in Table 3.

Thus, this method can give satisfactory results for the determination of copper in alloys by means of β-hydroxynaphthoic aldehyde. Copper was also determined in bronzes of various makes. Al^{3+}, Fe^{3+}, and Cr^{3+} ions were masked with tartaric acid.

0.1 g of test alloy containing copper was dissolved in nitric acid; the solution obtained was made up to 100 ml with water in a standard flask. To 10 ml of this solution was added 0.5 ml of 10% tartaric acid solution, 5 ml of alcohol, and 3 ml of 25% ammonia. The liquid was heated to the boil and then ~15 ml of 2% alcoholic solution of β-hydroxynaphthoic aldehyde added. The mixture was then re-heated until precipitate formed. After 25-30 minutes the precipitate was transferred to a No. 2 or No. 3 glass crucible, carefully washed 3-4 times with water, and dried at 115-120°. On standing, the solution gradually darkened and acquired a brownish color, this however did not seem to be reflected in the analytical results.

On determining copper in bronze containing 86.86% Cu, 8.71% Al, 2.62% Fe, 1.56% Mn, 0.14% Zn, we found 86.76, 87.97 and 86.44% Cu.

By introducing tartaric acid into solution, ions such as Fe^{3+}, Mn^{2+}, Al^{3+}, and Zn^{2+} did not interfere with copper determination. The method is distinguished by its simplicity and the rapidity with which it can be carried out. Determination of copper in the presence of nickel is impossible as the result of co-precipitation of the latter with β-hydroxynaphthoic aldehyde. It is necessary to remove nickel beforehand with dimethylglyoxime.

Determination of Copper in Malachite and Copper Sands

0.1-0.2 g of malachite was dissolved on heating in 0.5-1 ml of nitric acid (sp. gr. 1.40); water (10-15 ml) was then added. When an insoluble residue was obtained then the latter was filtered off, washed with hot water and the filtrate made up in a standard flask to 100 ml with water. In all cases 10 ml of test solution was taken; to this was added from 1 to 3 ml of 10% tartaric acid solution; the analysis was then carried out as described for bronze analysis. Results are given in Table 4.

For determination of copper in copper sands, aliquots of 0.5-2 g of test material, depending on the copper content, were boiled with 8 ml of HNO_3 (sp. gr. 1.40) for 10 minutes; the liquid was filtered off from insoluble material into a 100 ml standard flask; filter plus residue was carefully washed with hot water; the filtrate was made up to 100 ml with water. The procedure then followed was the same as that described for analysis of alloys. Results are given in Table 5.

TABLE 4

Number of malachite sample	Weight of aliquot	$C_{12}H_{14}O_4Cu$ in g	Cu found	
			in %	by electrolysis in %
1	0.1000	0.0344	53.87	53.75
	0.1000	0.0346	54.18	53.75
2	0.2000	0.0298	23.33	23.45
	0.2000	0.0302	23.65	23.45

TABLE 5

Number of sand sample	Weight of aliquot	Weight of precipitate $C_{22}H_{14}O_2Cu$ in g	Found Cu	
			in %	by electrolysis in %
1	2.0000	0.0226	1.77	1.78
	2.0000	0.0232	1.82	1.78
2	0.5000	0.0188	5.89	5.51
	0.5000	0.0186	5.82	5.51
3	2.0000	0.0270	2.11	1.73
	2.0000	0.0264	2.06	1.73
4	1.0000	0.0230	3.60	3.42
	1.0000	0.0230	3.60	3.42

SUMMARY

1. An inner complex salt formed between copper and β-hydroxynaphthoic aldehyde has been prepared and some of its properties studied.

2. A new semi-micro gravimetric method has been developed for the determination of copper in alloys and minerals, in which copper is weighed as $C_{22}H_{14}O_4Cu$ (conversion factor to $Cu^{2+} = 0.1566$).

3. Analysis is fairly accurate and rapid. Elements accompanying copper, such as, Fe, Mn, Al, and others can be kept in solution by means of tartaric acid.

Received March 25, 1955

LITERATURE CITED

[1] S. I. Gusev, V. I. Kumov and A. M. Stroganova, J. Anal. Chem., 10, 350 (1955) (T. p. 335)*.

---

* T. p. = C. B. Translation pagination.

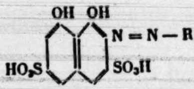
CHROMOTROPIC AZO DYES AS REAGENTS FOR TRIVALENT THALLIUM

I. M. Korenman, V. G. Potemkina and L. S. Fedorova

Gorky State University

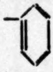
Comparatively few reagents are known at present for trivalent thallium. Among organic reagents one should mention methyl violet [1], dithizone [2], and benzidene [3].

We investigated the possibility of using certain chromotropic azo dyes as reagents for trivalent thallium:

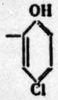


where R may be the following radicals:

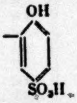
1



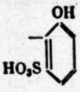
2



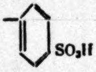
3



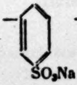
4



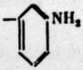
5



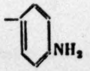
6



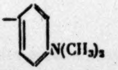
7



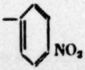
8



9



10



We used 0.1% aqueous solutions of these reagents; Reagent 8 was used in alcoholic solution. Reactions were carried out as follows: to 1 ml of a solution of a salt of trivalent thallium were added 0.1 ml of 2 N acetic acid and 1-2 drops of reagent solution. After shaking, the test tube plus solution was heated on a water bath for a few minutes at 35-40°. When the reaction was carried out in this way, all the chromotropic dyes gave color changes in the presence of trivalent thallium (Table 1).

Thus, all the reagents tested give color reactions with salts of trivalent thallium under the conditions indicated. The reactions will also occur in the cold, but slowly. Only Reagent 9 gives a positive reaction in hydrochloric acid media as well. Salts of univalent thallium do not give a positive reaction. Next we determined the limiting ratios at which thallium can be detected in the presence of other cations with Reagents 3, 6 and 9 (Table 2).

These results show that it is possible to detect thallium directly in the presence of other cations. In most cases, best limiting ratios were observed when Reagent 9 was used. Accordingly in subsequent experiments we concentrated entirely on the use of this reagent. We used this reaction for colorimetric determination of trivalent thallium salts. In a series of identical test tubes were placed 1 ml of standard solution, containing from 1 to 10 γ Tl^{3+}, and to each was added 0.1 ml of 2 N acetic acid, 4 drops of glycerol, and 3 drops of a 0.1% solution of Reagent 9. 1 ml of test solution was treated in exactly the same way, and the color obtained in this case compared with the colors of the series of standard solutions. Results of a large number of determinations showed that it is possible to get fully satisfactory results for the quantitative determination of 1-10γ of Tl^{3+} in 1 ml of solution, even in the presence of 100-1000 times its amount of aluminum, 100 times its amount of Fe^{3+}, 300 times its amount of Mg^{2+}, and 700 times its amount of Ca^{2+}.

TABLE 1

Reactions for Trivalent Thallium with Chromotropic Azo Dyes

Reagent number	Color		Limit of identification of Tl^{3+} in γ/ml	Limiting concentration
	Control	Tl^{3+}		
1	Rose	Yellow	2	1:500000
2	Rose	Yellow	1	1:1000000
3	Violet	Rose	5	1:200000
4	Rose	Yellow	3	1:330000
5	Rose	Yellow	1	1:1000000
6	Rose	Yellow	1	1:1000000
7	Rose	Yellow	25	1:40000
8	Rose	Yellow	10	1:100000
9	Blue	Violet	0.05	1:20000000
10	Rose	Yellow	20	1:50000

TABLE 2

Limiting Ratios in Detection of Thallium

Cation	Reagent			Cation	Reagent		
	3	6	9		3	6	9
	Limiting ratio of Tl^{3+} to cation				Limiting ratio of Tl^{3+} to cation		
Zr^{IV}	1 : 30	1 : 100	1 : 60	Mg^{2+}	1 : 900	1 : 100	1 : 10000
La^{3+}	1 : 100	Does not interfere	1 : 1000	Ca^{2+}	1 : 400	1 : 100	1 : 4000
Ce^{3+}	1 : 400		1 : 5000	Mn^{2+}	1 : 500	1 : 150	1 : 5000
Al^{3+}	1 : 200	1 : 850	1 : 200	Co^{2+}	1 : 10	1 : 10	1 : 50
Cr^{3+}	1 : 20	1 : 1	1 : 900	Ni^{2+}	1 : 20	1 : 100	1 : 5000
Fe^{3+}	1 : 10	1 : 20	1 : 5000	Cu^{2+}	1 : 200	1 : 100	1 : 5500
Bi^{3+}	1 : 900	1 : 800	1 : 6000	Zn^{2+}	1 : 20	1 : 20	1 : 100
UO_2^{2+}	1 : 100	1 : 100	1 : 300	Hg^{2+}	1 : 1300	Does not interfere	1 : 5000
Be^{2+}	1 : 40	Does not interfere	1 : 600	Pb^{2+}	1 : 1200		1 : 4500

SUMMARY

1. It has been shown that chromotropic dyes give characteristic and very sensitive reactions with trivalent thallium. Univalent thallium salts do not give these reactions.

2. Some of the reagents tested permit determination of trivalent thallium salts without preliminary isolation in the presence of a large excess of certain other cations.

The reactions described for thallium can be used for the colorimetric determination of small amounts of thallium.

Received May 27, 1954

LITERATURE CITED

[1] V. I. Kuznetsov, J. Anal. Chem., 2, 179 (1947).

[2] A. T. Pilipenko, J. Anal. Chem., 5, 7 (1950).

[3] "Reactions and Reagents", Edited by A. S. Komarovsky, 1950, p. 139.

BLANK
PAGE

POLAROGRAPHIC DETERMINATION OF ACRYLONITRILE IN AQUEOUS-ALCOHOL SOLUTIONS

M. N. Platonova

S. M. Budenny Engineering Academy of Communications

The nitrile of acrylic acid is widely used as a basic raw material for the industrial production of various highly polymerized products. A rapid quantitative method of determining acrylonitrile is accordingly essential for the study and control of its polymerization processes.

The methods described in the literature – spectrophotometric [1], and spectroscopic [2] – for determination of acrylonitrile in solutions require special apparatus, which is not always available in an ordinary laboratory. The method of determining acrylonitrile by means of cyanoethylation is rather complicated [3].

Polarography has recently started to be used in industry for the quantitative determination of organic materials on a fairly wide scale. A visual apparatus for this purpose, can be assembled in any chemical laboratory by a suitable choice of resistances, as long as a sensitive enough galvonometer is available. The work described in the present article is devoted to the application of a polarographic method for the determination of acrylonitrile in aqueous solutions.

A method has been published for the polarographic determination of acrylonitrile [4], but the relation between diffusion current and concentration was not studied over a wide enough range by the authors (from only 13-3 mm/liter). Accordingly we studied this relation over a wider concentration range (approximately the range found during production control of polymerization processes); in addition, we studied the mechanism of the reduction of acrylonitrile on a dropping mercury electrode.

TABLE 1

Concentration of acrylonitrile in mM/liter	Wave height in μA	Diffusion current constant $I_d = \frac{i_d}{m^{2/3}t^{1/6}c}$
12,04	33,01	3,42
6,02	16,45	3,41
3,01	8,35	3,47
1,50	3,90	3,25
0,75	1,82	3,03
0,375	1,00	3,32

Mean value 3.31

EXPERIMENTAL

Work was carried out on a visual polarograph assembled in the laboratory on the usual principle.

The parameters of the M 21/1 galvanometer used were: $R_{VN} = 780\Omega$; $R_{KR} = 68{,}000\Omega$; the intensity of the galvanometer with respect to current was $0.664 \cdot 10^{-10}$ A/mm of the scale at a distance of 1.5 meters; the capillary characteristic was: $L = 1.25\ mg^{2/3}\ sec^{-1/2}$ at zero potential. The supporting electrolyte consisted of 0.01 M $(C_2H_5)_4NCl$ in 1 liter of 50% ethyl alcohol, since, as was shown experimentally, it is necessary to use aqueous-alcohol mixtures for determination of acrylonitrile. The residual current in this electrolytic solution did not exceed 0.3-0.5 μA. A layer of mercury at the bottom of the electrolyzer served as anode, its potential on being measured with respect to a calomel electrode was found to be equal to +0.033 V.

In order to construct a calibration curve, solutions of acrylonitrile were prepared in which the concentration of the latter was varied from 12.04 to 0.3 mM/liter in the supporting electrolyte described above. The acrylonitrile was freshly distilled, and had a boiling point of 77°.

Examples of the polarograms obtained for acrylonitrile are shown in Fig. 1.

The results obtained, corrected for residual current are given in Table 1 (t = 23°).

It is clear from these results, that within the concentration range studied there is a linear relation between wave height and concentration. The half-wave potential of acrylonitrile was calculated by means of the equation for a polarographic wave [5].

Fig. 2 shows the curve relating logarithm i/(I-i) to the potential of the dropping mercury electrode for c = 1.5 mM/liter of acrylonitrile. Values of the half-wave potential, relative to higher concentrations are given in Table 2.

TABLE 2

c of acrylonitrile in mM/liter	$E_{1/2}$ relative to the saturated calomel electrode in V
6.02	2.05
3.01	2.05
1.50	2.05

The results in Table 2 show that the half-wave potential of acrylonitrile is independent of concentration, if a correction is applied for the drop in potential in the electrolyzer itself.

On Fig. 3 is shown the calibration curve by means of which it is possible to carry out a quantitative determination of acrylonitrile in aqueous-alcohol solutions. On the basis of the equation for the half-wave potential it is possible to calculate the number of electrons which participated in the reaction. This number proved to be equal to 0.59, which indicates an irreversible character for the reduction of acrylonitrile on a dropping mercury electrode.

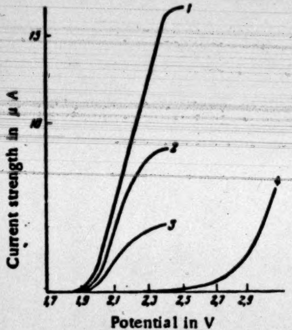


Fig. 1. Polarogram for solutions of acrylonitrile of various concentrations: 1) 6.04 mM/liter; 2) 3.02 mM/liter; 3) 1.51 mM/liter.

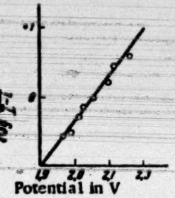


Fig. 2. Relation between log i/(I-i) and potential of the dropping mercury electrode for the acrylonitrile wave c = 1.51 (relative to the saturated calomel electrode).

The number of electrons participating in the reaction can also be determined by using the approximate value of the diffusion coefficient, calculated from formula [5]:

$$D = \frac{3,32\cdot 10^{-5}}{V^{1/3}} \text{cm}^2\cdot\text{sec}^{-1}, \qquad (1)$$

where V is the molecular volume of the dissolved material.

This formula can be used on the assumption that the molecule of acrylonitrile is hydrated to a slight extent and has a spherical form

$$V = \frac{M}{d} = \frac{53}{0,800} = 66,3 \text{ cm}^3/\text{mol.}, \qquad (2)$$

where 53 is molecular weight of acrylonitrile, while 0.800 is its density at 25°. Substituting this value in Formula (1) we get an approximate value for the diffusion coefficient of acrylonitrile:

$$D = \frac{3{,}32\cdot 10^{-5}}{(66{,}3)^{1/3}} = 0{,}82\cdot 10^{-5}\ cм^2\cdot \mathrm{sec}^{-1}$$

from which

$$n = \frac{i_d}{605 D^{1/2} m^{2/3} t^{1/6} c} =$$

$$= \frac{8{,}45}{605\,(0{,}82\cdot 10^{-5})^{1/2}\cdot 1{,}25\cdot 3{,}02} =$$

$$= 1{,}65 \approx 2.$$

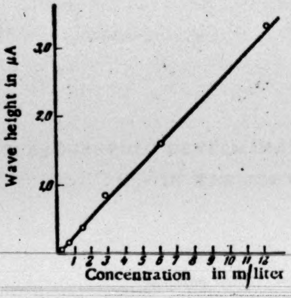


Fig. 3. Relation between wave height and concentration in an aqueous-alcohol solution on tetraethylammonium chloride.

The calculations adduced enable one to conclude that two electrons participate in the electrochemical reaction. This conclusion permits one to suggest that during the reduction of acrylonitrile on a dropping mercury electrode hydrogen attaches to the double-bond to form the nitrile of acetic acid, according to the equation:

$$CH_2 = CH - C \equiv N + 2e + 2H^+ \rightarrow CH_3 - CH_2 - C \equiv N.$$

SUMMARY

1. The wave height of acrylonitrile in a 0.01 M aqueous-alcoholic solution of tetraethylammonium chloride has been shown to be proportional to nitrile concentration over the range 0.3 to 12.04 mM/liter.

2. Reduction of acrylonitrile on the dropping mercury electrode is irreversible.

3. The number of electrons which participate in the reaction has been calculated, and a mechanism for the reduction of acrylonitrile is suggested.

Received June 9, 1955

LITERATURE CITED

[1] H. Brieger and F. Rieders, Arch. Ind. Hyg. Occupational Med., 6, 128 (1952).

[2] I. D. Sands and G. S. Turner, Anal. Chem., 24, 791 (1952).

[3] A. P. Terentyev, P. F. Butskus and V. G. Yashunsky, J. Anal. Chem., 9, 3 (1954) (T. p. 1)*.

[4] W. L. Bird and C. H. Hale, Anal. Chem., 3, 24, No. 3, 586-587 (1952).

[5] I. Kolthoff, "Polarography", 1948, pp. 62 and 150.

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

POLAROGRAPHIC DETERMINATION ON SOLID ELECTRODES OF HEAVY METALS IN THE AIR OF INDUSTRIAL ESTABLISHMENTS

I. B. Kogan

Ukrainian Central Institute for Labor and Professional Disease Hygiene

During recent years Soviet scientists have developed a number of theoretical propositions in the field of polarography on solid electrodes.

The work of Skobets and others [1-7], has demonstrated the possibility of a practical application of solid electrodes in analytical practice. The advantages of solid electrodes over the dropping mercury electrode, and also the potential use of solid electrodes in anodic polarography have enabled quantitative determinations of small amounts of harmful materials to be carried out.

Our work was carried out on a "Geological prospecting polarograph" with automatic recording of I-V curves. The solid micro-cathode was made from platinum wire fused into a glass tube. A drop of silver was welded onto the platinum wire. A silver plate served as anode. The cathode was fixed in a metal tube, fitted in its turn into two ball bearings. The micro-cathode was rotated by means of a synchronous motor; this ensured uniform rotation. The rotation rate was 700-750 revolutions/minute. For a given rotation rate of the electrode, a limiting diffusion current was obtained as well as instantaneous stabilization of the current with time on the rotating electrode. The silver electrodes were amalgamated before each test by immersion in pure mercury.

Determination of Cadmium Oxide in the Air

Determination of cadmium oxide which one meets in non-ferrous metallurgy, smelting of zinc, etc. is of interest in industrial hygiene chemistry. The limiting permissible amount of cadmium oxide is 0.0001 mg/liter of air. Analysis of cadmium salts was carried out using 0.2 N ammonia as supporting electrolyte. Oxygen was removed from solution by addition of 0.2 g of sodium sulfite. Amalgamated silver plate 2 cm^2 in area served as anode. Known amounts of cadmium chloride were introduced into the electrolyzer, supporting electrolyte added, followed by 0.2 g of sodium sulfite. After 10 minutes the amalgamated electrodes were immersed in the solution, the cathode rotated at a rate of 700-750 revolutions/minute, and polarograms taken. All measurements were carried out with a galvanometer sensitivity of 1/5. On Fig. 1 are shown polarograms for solutions of varying concentrations of cadmium chloride using a rotating amalgamated silver cathode.

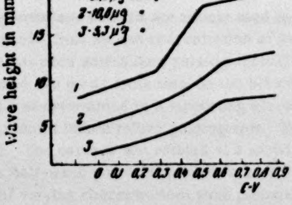


Fig. 1. Polarogram of cadmium chloride in a supporting electrolyte of 0.2 N ammonia.

The half-wave potential of cadmium in a supporting electrolyte of 0.2 NH_4OH was 0.51 V (with respect to the saturated calomel electrode). The tests carried out showed that reproducible results can be obtained (Table 1).

The aerosol of cadmium oxide was sampled into a five-liter evacuated flask. The air sample was treated with 0.2 N HNO_3 and left to stand for 30 minutes with frequent shaking. The contents of the bottle were transferred to a porcelain basin; the flask was rinsed 2-3 times

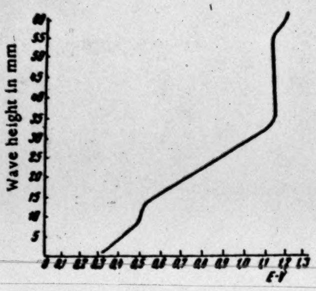


Fig. 2. Polarograms of copper and zinc when both are simultaneously present.

TABLE 1

Determination of Cadmium on a Rotating Solid Electrode

Cadmium taken in μg	Cadmium found in μg	% Determined
10,65	12,5	117
2	2	100
21,32	21,0	98
5,32	5,5	103

with 5 ml of water and the whole evaporated to dryness. The dry residue was treated 3 times with distilled water, evaporation to dryness being carried out after each treatment. The dry residue was finally treated with ammonia solution and transferred to the electrolyzer. The minimum amount of cadmium that could be determined amounted to 2 μg; the accuracy of the method is 5-10%.

Separate Determination of Zinc and Copper Oxides in Air

Separate determination of zinc and copper oxides in air presents a number of difficulties. Determination of zinc oxide has been studied by many authors [8, 9]. The half-wave potential of zinc is 1.2 V, while that of copper is 0.4 V (relative to the saturated calomel electrode) when the supporting electrolyte is ammonia. This fact, undoubtedly, plays a decisive part in the determination of the cations indicated when both are simultaneously present in the air. Tests were carried out with solutions of $CuSO_4$ in 0.2 N ammonia as supporting electrolyte. On Fig. 2 are shown polarograms of Cu^{2+} and Zn^{2+} when they were determined simultaneously. In order to carry out quantitative determinations of Cu^{2+} and Zn^{2+}, calibration curves were drawn for each cation in solutions of their respective salts, and test concentrations determined by means of these curves. Table 2 contains the results for separate determination of Cu^{2+} and Zn^{2+} on a solid electrode at a galvanometer sensitivity S = 1/5. Polarograms were taken by means of the method described above for cadmium oxide.

TABLE 2

Separate Determination of Cu^{2+} and Zn^{2+} on a Solid Rotating Cathode

Taken in μg		Found in μg		% Determined		Taken in μg		Found in μg		% Determined	
Cu^{2+}	Zn^{2+}	Cu^{2+}	Zn^{2+}	Cu^{2+}	Zn^{2+}	Cu^{2+}	Zn^{2+}	Cu^{2+}	Zn^{2+}	Cu^{2+}	Zn^{2+}
12	18	12	17,5	100	97	5	3	5	3	100	100
8	12	7,5	12,5	94	104	5	10	4,5	10	90	100
10	10	10	10	100	100	12	18	12	17,6	100	98

Determination of Manganese in Air

Manganese and its salts are widely used in machine construction, metal working, the mining industry, etc. The permissible limit for the concentration of manganese in air is 0.0003 mg/liter according to NSP-101-51. Manganese has been determined polarographically by a few authors [10-12]. In order to increase the sensitivity of the method, we made some tests on the behavior of manganese on a solid rotating drop-shaped silver electrode. Manganese was determined in a supporting electrolyte of 0.2 N KCNS. Hydrogen was passed through the solution for 10-15 minutes before taking polarograms. The total volume of the liquid being analyzed polarographically was 1.5 ml. The cathode was rotated at a speed of 800 revolutions/minute. Galvanometer sensitivity used was 1/20. The half-wave potential proved to be 1.5 V (with respect to the saturated calomel electrode). Solutions of $MnSO_4$ of varying concentrations were prepared in order to get a calibration curve.

Table 3 contains the results for polarographic determination of Mn in a supporting electrolyte of KCNS.

TABLE 3

Quantitative Determination of Manganese on a Solid Electrode

Taken in μg	Found in μg	% Determined	Taken in μg	Found in μg	% Determined
7	7	100	8	7,6	95
5	5	100	9	8,6	95
10	10,1	101	8	8,6	95
4	4	100	3	2,5	83
			6	6,5	108

Manganese in the air was trapped in a dust tube filled with hygroscopic cotton wool; the latter was given a preliminary treatment with 5% HNO_3, carefully washed with water to a neutral reaction with litmus, and dried in a drying oven. After taking test air samples, the cotton wool was removed from the tube, placed in a porcelain crucible and ignited in the crucible over a small flame of an alcohol burner. The residue was calcined at 600° in a muffle. The ash was dissolved in 1 ml of concentrated HNO_3 (sp. gr. 1.4), and the solution evaporated to dryness on a water bath. 5 ml of distilled water was added to the residue and the whole re-evaporated to dryness. This operation was repeated until the residue was neutral. The clear neutral solution was transferred from the crucible to the electrolyzer, and polarograms were taken by the method described above.

If a manganese content of more than 5 μg per liter of air is expected, samples can be taken in an evacuated 5 liter flask. Absorption of manganese is effected by 5 ml of HNO_3; subsequent procedure is then the same as that described above. The method developed for manganese determinations is simple and convenient. The sensitivity of the method is 1-2 μg of manganese in 1.5 ml of solution; the accuracy of the method is 10%

Quantitative Determination of Chromates in Air

Chromates have found wide application in machine construction, the airplane, leather, textile, dye, and other industries.

The permissible limit of chromic anhydride, chromates, and dichromates is equal to 0.0001 mg/liter (the norm for planning industrial enterprises, NSP 101-51).

Our problem was to develop a sensitive method for determining chromates in the air of industrial enterprises.

Reduction of chromate ions on the dropping mercury electrode has been studied by Lingane and Kolthoff [13-14]. They assume that reduction proceeds as follows:

$$CrO_4^{2-} + 4H_2O + 3e \rightarrow Cr(OH)_3 + 5OH^-$$

$$CrO_4^{2-} + 2H_2O + 3e \rightarrow CrO_2 + 4OH^-.$$

The reaction occurs in alkaline media. In neutral and non-buffered solutions, the polarogram for chromate consists of several waves.

We studied the behavior of chromate ions on solid amalgamated silver electrodes. Well-defined waves were obtained in a supporting electrolyte of 0.1-1N NaOH. On Fig. 3 are shown the characteristic waves obtained for chromate ions.

In order to determine chromate quantitatively, an aliquot of potassium chromate was dissolved in water. To the aqueous chromate solution was added 0.1 N NaOH. The total amount of the liquid to be polarographed was 2 ml. Sodium sulfite (0.2 g) was added to the alkaline chromate solution in the electrolyzer, and after 10 minutes polarograms were taken.

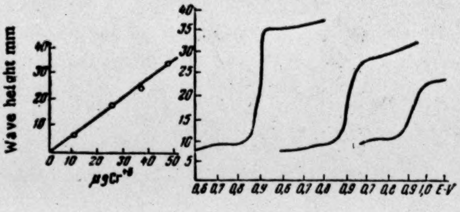


Fig. 3. Polarograms for chromate ions in 0.1 N NaOH as supporting electrolyte.

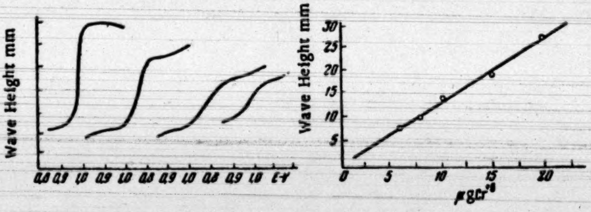


Fig. 4. Polarograms and calibration curve for CrO_3.

Determination was carried out on the basis of the reduction wave for Cr^{VI}. Electrolytic reduction of chromium from an alkaline solution of chromate gives a well-defined wave at a potential within the limits of 0.9-1.0 V.

Positive results were not obtained on taking polarograms of chromate ions in acid solutions; the reduction potential of the chromate ion is displaced to more negative values, and the chromate wave fuses with that of hydrogen. A calibration curve constructed for chromate in a supporting electrolyte of 0.1 N sodium hydroxide, in the presence of sulfite, shows a linear relationship between diffusion current and chromium concentration in solution (Fig. 3).

Similar results were obtained for chromium determinations in dichromate solutions. The Cr^{VI} wave is well defined in dichromate solutions. The chromium wave in an alkaline solution of dichromate, as well as the calibration curve, are similar to those for chromate solutions. Chromium anhydride (CrO_3) is widely used in electrolytic chrome plating; we studied the possibility of determining it quantitatively, on a solid amalgamated silver electrode. Tests were carried out in 0.1 N NaOH as supporting electrolyte, in presence of Na_2SO_3. Polarograms were taken under the conditions used for chromate and dichromate. The calibration curve was made with recrystallized CrO_3. Fig. 4 shows the calibration curve and polarograms for CrO_3.

Results for the polarographic determination of chromium in solutions of chromic anhydride are given in Table 4.

Aerosols of chromic acid and its salts can be trapped from the air in a dust tube, consisting of two cylindrical tubes. The inner tube is connected via a ground glass joint to the outer one. Filter paper is fitted to the end of the inner tube. Two samples are taken at each sampling point. 50-100 liters of air are sucked at the rate of 5-10 liter/minute using a vacuum pump and rheometer.

After sample taking, the filter paper was removed from the tube and placed in a porcelain basin. The tube was washed with a few portions of hot distilled water, this water being added to the basin containing the filter paper. The liquid was transferred to another basin. This operation was repeated 3-4 times. The liquid was then evaporated on a water bath to 3-4 ml. It was poured from this basin into a cylinder, the basin was washed with hot water and the washings added to the same cylinder. 1 ml of test liquid was used for polarographic measurements; the procedure employed was the same as that described above.

TABLE 4

Results for the Polarographic Determination of CrO_3

Taken in µg	Found in µg	% Determined
34.46	37.5	108
27.5	26.25	95
24.1	27.5	114
20.6	22.5	108
13.78	15.75	114

SUMMARY

1. Polarographic analysis of small concentrations of heavy metals in air can be successfully carried out on solid rotating silver amalgamated cathode and anode.

2. Methods have been developed for the quantitative determination of Cu^{2+} and Zn^{2+}, Cd^{2+} and Mn^{2+} in air.

3 A method has been developed for the separate determination of Cu^{2+} and Zn^{2+} in air when they are simultaneously present.

4. A polarographic method for determining chromates in air has been developed.

5. The sensitivity of the methods developed amounts to 1-2 µg in 2 ml of liquid (the accuracy of the method is 10-15 %).

Received July 14, 1954

LITERATURE CITED

[1] E. M. Skobets and S. A. Kacherova, Factory Lab., 13, 133 (1947).

[2] E. M. Skobets, L. S. Berenblyum and N. I. Atamanenko, Factory Lab., 14, 131 (1948).

[3] E. M. Skobets, P. P. Turov, and V. D. Ryabokon, Factory Lab., 14, 772 (1948).

[4] E. M. Skobets, P. P. Turov, and V. D. Ryabokon, Factory Lab., 15, 912 (1949).

[5] E. M. Skobets and N. I. Atamanenko, Factory Lab., 13, 1291 (1949).

[6] E. M. Skobets, Trans. Second All-Union Conference on Electrochem., 1949, p. 341.

[7] M. S. Lyalikov and V. I. Karmazin, Factory Lab., 14, 138 (1948).

[8] N. Ya. Khlopin, Factory Lab., 14, 2 (1948).

[9] I. V. Kogan, Factory Lab., 16, 932 (1950).

[10] Yu. S. Lyalikov, Trans. All-Union Conference on Analytical Chemistry, 2, 1948, p. 439.

[11] A. Portnov and G. Sushentsov, Factory Lab., 10, 41 (1941).

[12] I. B. Kogan and S. L. Makhover, J. Sanitation and Hygiene No. 2, 52 (1954).

[13] J. J. Lingane and I. M. Kolthoff, J. Am. Chem. Soc., 62, 852 (1940).

[14] E. A. Korshunov and M. K. Shchennikova, Factory Lab., 13, 682 (1947).

BLANK
PAGE

KINETIC METHODS OF QUANTITATIVE ANALYSIS

PART III. DETERMINATION OF SMALL AMOUNTS OF MOLYBDENUM*

K. B. Yatsimirsky and L. P. Afanaseva

Ivanov Chemico-Technical Institute

The reaction $H_2O_2 + 2I^- + 2H^+ = 2H_2O + I_2^-$ only proceeds slowly at room temperature, and in the absence of catalysts. Some research workers [1, 2], have established that it obeys the bimolecular rule; its rate depends also on hydrogen ion concentration and foreign neutral salts. The presence in solution of very small amounts of molybdenum, tungsten, iron, vanadium, and other materials which can combine with hydrogen peroxide, speed up this reaction considerably [3, 4]; it has accordingly been used by us for developing a method for determining small amounts of molybdenum.

EXPERIMENTAL

The stock solutions used were: 0.01 M H_2O_2, 0.01 M KI, 4M H_2SO_4, starch solution, and a solution of ammonium molybdate containing 0.87×10^{-6} g/ml of Mo. The solutions of hydrogen peroxide, sulfuric acid, and starch were prepared from chemically pure materials. The potassium iodide was twice recrystallized from alcohol. The purity of the stock solutions was checked by measuring the reaction velocity under conditions described in the literature [2]. The fact that identical results were obtained testified to the absence of any appreciable amount of catalyzing impurities. The ammonium molybdate was analyzed by calcining at 300-400° and weighing the residue to MoO_3.

Into a 50 ml standard flask were introduced solutions of potassium iodide, sulfuric acid, water, and starch (the purity of the KI was once again established during this procedure), followed by the hydrogen peroxide and ammonium molybdate solutions. The mixture thus prepared was made up to the mark with distilled water and carefully mixed. The concentrations of the reactants in the flask after mixing were as follows: KI-0.0002 M, H_2SO_4-0.08 M, H_2O_2-0.001 M, ammonium molybdate (calculated as molybdenum) from $1.7 \cdot 10^{-8}$ g/ml to $8.7 \cdot 10^{-8}$ g/ml.

The solution was placed in the cell of an FM photometer, and 3 minutes after mixing, optical density was measured every minute using a N5 light filter (effective wave-length 553 mμ). On the basis of results obtained graphs were constructed of time — optical density; tangent of each line characterizing the reaction velocity of iodide oxidation was then determined (Fig. 1). All experiments were carried out at a temperature of 20-21°. During observation time not more than 6% KI and 1% H_2O_2 reacted. A curve was constructed of Mo concentration (tangent of the straight line); all points on this curve fall on one straight line (Fig. 2).

In order to find out the effect of acidity on the rate of the reaction being studied, various amounts of sulfuric acid were added to a reaction mixture consisting of $2 \cdot 10^{-4}$ mol/liter of KI, 10^{-3} mol/liter of H_2O_2 and $6 \cdot 10^{-7}$ mol/liter of molybdate. The relation between reaction velocity and amounts of sulfuric acid is shown in Fig. 3.

---

* Part II. J. Anal. Chem. 10, No. 6, p. 344 (1955).

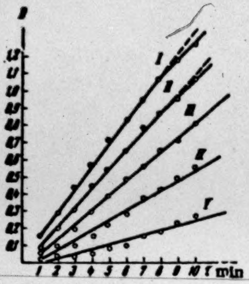


Fig. 1. Change of optical density in the system H_2O_2-KI-$(NH_4)_2MoO_4$.
Molybdate concentration in terms of molybdenum:
I) $8 \cdot 10^{-8}$ g/ml; II) $6 \cdot 10^{-8}$ g/ml; III) $4.3 \cdot 10^{-8}$ g/ml; IV) $2.4 \cdot 10^{-8}$ g/ml; V) $2.4 \cdot 10^{-8}$ g/ml.

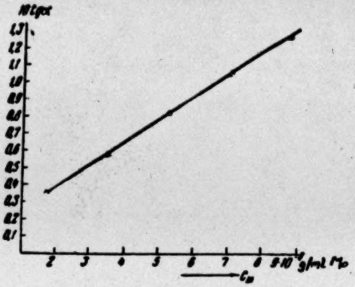


Fig. 2. Relation between reaction velocity (I) and molybdenum concentration.

TABLE 1

Determination of Molybdenum on the Basis of Kinetic Results

Molybdate concentration in mol/liter	Molybdate found in mol/liter	Deviation in %
$4.86 \cdot 10^{-7}$	$4.48 \cdot 10^{-7}$	− 7.8
$4.50 \cdot 10^{-7}$	$4.80 \cdot 10^{-7}$	+ 6.7
$2.96 \cdot 10^{-7}$	$3.19 \cdot 10^{-7}$	+ 7.8
$1.91 \cdot 10^{-7}$	$1.89 \cdot 10^{-7}$	− 1.0

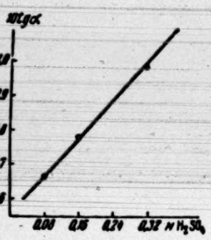


Fig. 3. Relation between reaction velocity (I) and H_2SO_4 concentration.

Four solutions were prepared each containing different amounts of ammonium molybdate; the amount of molybdenum was then determined in these solutions by measuring the reaction rate of iodide oxidation by hydrogen peroxide and using graph 2.

The results obtained are shown in Table 1

Finally, in order to determine the effect of various impurities on the accuracy of determination of molybdenum, various salts in concentrations ranging from $1.6 \cdot 10^{-4}$ M to $8.2 \cdot 10^{-4}$ M were added to test solutions (H_3PO_4 was used at a concentration of 10^{-2} M). Under these conditions, the concentration of test ion exceeded that of molybdenum by a few hundred times (from 250 to 1300 times as much). The results obtained are given in Table 2.

DISCUSSION OF RESULTS

The reaction rate of hydrogen peroxide with iodide in an acid medium, in the presence of molybdate, can be expressed to a first approximation, by the following equation:

$$\frac{d[I_2]}{dt} = \kappa c_{Mo} c_{H_2O_2} c_{I^-}, \qquad (1)$$

where κ is the catalytic coefficient, c_{H_2O}, c_{I^-}, and c_{Mo}, respectively, are the concentrations of hydrogen peroxide, iodide, and molybdate. It is possible that in acid media, molybdate may be partially converted into MoO_2^{2+} and other forms.

TABLE 2

Effect of Other Materials on Molybdenum Determination
(Concentration $6 \cdot 19^{-7}$ mol/liter Mo)

Other ion	Concentration of other ion in mM/liter	Ratio of concentration of other ion to molybdenum concentration	Tangent of the straight line t-D	Other ion	Concentration of other ion in mM/liter	Ratio of concentration of other ion to molybdenum concentration	Tangent of the straight line t-D
	—	—	$0.84 \cdot 10^{-1}$	Cr^{3+}	0.38	630	$0.88 \cdot 10^{-1}$
Co^{3+}	0.94	570	$0.84 \cdot 10^{-1}$	Cd^{2+}	0.16	250	$0.58 \cdot 10^{-1}$
Ni^{3+}	0.34	570	$0.80 \cdot 10^{-1}$	Hg^{2+}	0.50	830	$0.30 \cdot 10^{-1}$
Cu^{2+}	0.31	520	$0.80 \cdot 10^{-1}$	VO_3^-	0.20	330	$1.03 \cdot 10^{-1}$
Ca^{2+}	0.50	830	$0.84 \cdot 10^{-1}$	$H_3AsO_4^-$	0.27	450	$0.00 \cdot 10^{-1}$
Mg^{2+}	0.82	1330	$0.84 \cdot 10^{-1}$	Silicate	1.0	—	$0.00 \cdot 10^{-1}$
Mn^{2+}	0.38	630	$0.84 \cdot 10^{-1}$	$H_2PO_4^-$	5.0	—	$0.70 \cdot 10^{-1}$
Zn^{3+}	0.31	520	$0.84 \cdot 10^{-1}$				

Actually, as is evident from the graphs adduced, the relation between reaction velocity and molybdenum concentration is somewhat more complicated and is better expressed by the equation:

$$\frac{d[I_2]}{dt} = \kappa c_{Mo} c_{H_2O_2} c_I + \text{const.} \qquad (2)$$

The value of the constant in equation (2) is not large. The catalytic coefficient as determined from equation (1) is equal to $1.4 \cdot 10^8$ (time in minutes, concentration in moles/liter).

On the basis of theoretical considerations which we advanced in our first paper [5], it is possible to estimate the minimum concentration of molybdenum which can be detected by this method. For this purpose it is necessary to know the velocity constant for the non-catalyzed reaction. Under our conditions this value, according to published results, whould be equal to 3.68, from which:

$$c_{Mo_{min}} \geq 0.1 \frac{k}{\kappa} = 2.6 \cdot 10^{-9} \text{ M}. \qquad (3)$$

Consequently, the method which we have suggested is far more sensitive than any method hitherto known for determining molybdenum.

The experiments described here for molybdenum determination were carried out at higher concentrations (from $1.8 \cdot 10^{-7}$ M to $9.1 \cdot 10^{-7}$ M), this corresponds to a range of from 0.17 to 0.87 μg per10 ml. These concentrations are also considerably lower thah those used for colorimetric analysis. In this molybdenum concentration range, reproducibility is 10%. When the method described here (for determinating molybdenum concentrations) is used, there is no need to introduce corrections for the velocity of the non-catalyzed reaction; this simplifies the analytical method appreciably.

Experiments which we carried out demonstrated the possibility of determining molybdenum at even lower concentrations; however, the reproducibility drops off significantly. This is connected with the fact that at very low molybdenum concentrations, impurities play a very essential role — complete freedom from silicate is impossible when glass apparatus is used. Presumably, lower concentrations could be handled if the effect of silicate could be completely eliminated.

The reaction rate of oxidation of iodide by hydrogen peroxide depends on hydrogen ion concentration. With increasing acid concentration in solution, reaction rate increases. It is possible that in the given instance, formation of the hydroperoxonium ion $H_3O_2^+$, which reacts more vigorously with iodide, occurs.

Determination of molybdenum by the method suggested is possible in the presence of many other metals. Cobalt, nickel, copper, calcium, magnesium, manganese, zinc, chromium (trivalent) have no significant effect on reaction velocity at the concentrations studied. In the presence of vanadate there is an appreciable increase in reaction rate; this, apparently, can be explained by the formation of a complex between vanadate and hydrogen peroxide. Reaction rate also increases in the presence of tungstate. Materials which oxidize iodide should also be absent. Slowing down of the reaction by mercury and cadmium ions is related to the fact that these elements form complexes with iodide and lead to a sharp decrease in its concentration. Phosphate slows down the reaction; in the presence of silicate and arsenate, in general, no evolution of iodine is observed. All these ions form complexes with molybdate and suppress its catalytic activity sharply.

The practical absence of oxidation of iodide by hydrogen peroxide in dilute solutions, in the presence of molybdate and silicate or arsenate can be used for detection of these two latter ions in qualitative analysis. It is possible in this way to detect very small amounts of arsenate and silicate.

SUMMARY

A new method is suggested for the determination of small amounts of molybdenum; it is based on making use of the catalytic effect of molybdate on the oxidation of iodide by hydrogen peroxide. The method has been checked in the concentration range $1.8 \cdot 10^{-7}$ to $9.1 \cdot 10^{-7}$ M.

The effect of other materials on the accuracy of determination has been studied.

Received January 11, 1955

LITERATURE CITED

[1] A. A. Noyes and W. O. Scott, Z. Phys. Chem. 18, 118 (1895).

[2] F. Bell and R. Jill, J. Phys. Colloid Chem. 55, 874 (1951).

[3] J. Brode, Z. Phys. Chem. 37, 257 (1901).

[4] E. I. Orlov, J. Russ. Phys. Chem. Soc. 45, 489 (1913).

[5] K. B. Yatsimirsky, J. Anal. Chem. 10, 339 (1955), (T. p. 323)*.

---

* T. p. = Consultants Bureau Translation pagination.

CEMENTATION OF CERTAIN METALS BY ZINC AMALGAM

E. F. Speranskaya

S. M. Kirov Kazakh State University

In recent years interest in developing amalgam methods of quantitative separation and determination of metals has increased, as well as the search for amalgam methods suitable for hydrometallurgical treatment of poor ores with the aim of using their components.

As Hohn [1], has pointed out, the method of amalgam metallurgy is particularly important for treating poor ores.

One of the fundamental stages in amalgam metallurgy is cementation (phase exchange) with amalgams. Without dwelling on the theory of the cementation process, which has been discussed in detail in a series of papers by Kozlovsky and coworkers [8, 9], we note that for the purposes of cementation, the most suitable amalgams are those of the metals: zinc, cadmium, tin, lead, and bismuth. These metals dissolve readily in mercury without reacting chemically with it; as a result, their deposition potentials on mercury do not differ from their deposition potentials on solid cathodes. The most active amalgam of the group of metal amalgams indicated, is that of zinc. Zinc amalgam has been used by many authors [2-4], for quantitative separation of metals, and for cementation of metals which interfere with the determination of anions in sparingly soluble and complex salts, for determination of metals by the method of internal electrolysis [5], and also in volumetric analysis as a reducing agent [6, 7].

It should be noted however, that no systematic studies have been carried out on the cementing capacity of zinc amalgam as applied to certain metals.

In the investigation described in the present article we studied cementation of copper, cadmium, lead, antimony, nickel and iron by zinc amalgam, as follows:

A. The quantitative ratios of the cathode-reducing metals to anode-oxidizing zinc were determined.

B. The effect of concentration and electrolyte composition on the rate of the process was established, and the percentage efficiency of the zinc determined.

Cementation was carried out in solutions of sulfuric and hydrochloric acids, and in ammonia solution.

In the first series (a) of experiments, 0.1 M solutions of the acids indicated and 0.1-1 M ammonia solutions were used. Concentrations of the zinc amalgam were varied within the limits 2 to 7%.

In the second series (b), the amalgam concentration was kept constant (2%), while the concentration of electrolyte was changed (0.01-1 M).

The first series of experiments were carried out by shaking a solution containing the metals to be cemented in amounts equivalent to the zinc, in a separating funnel. Completness of deposition of the metals was controlled by using the appropriate qualitative reactions for the various metals: copper – potassium ferrocyanide, lead – sodium sulfide, cadmium – sodium sulfide, antimony – hydrogen sulfide, nickel – dimethylglyoxime, and iron – potassium ferricyanide.

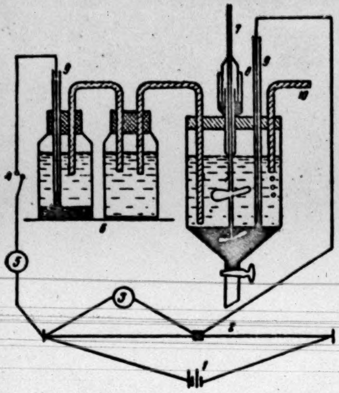


Fig. 1. Schematic diagram of the apparatus for metal cementation.
1) Accumulator; 2) rheocord; 3) voltmeter; 4) key; 5) galvanometer; 6) half-element; 7) stirrer; 8) mercury seal; 9) contacts; 10) tube for hydrogen.

The second series of tests was carried out in the apparatus shown schematically in Fig. 1. In the vessel was placed 70 ml of solution, containing in all cases 0.05 g of the cemented metal in hydrochloric, sulfuric or ammonia of a definite concentration, and then amalgam introduced. Cementation was effected by stirring the amalgam and solution with a glass stirrer in a hydrogen atmosphere. The stirrer was rotated at a speed of 400 revolutions/minute.

Cementation stopped after 15 minutes. The solution was separated from the amalgam and analyzed for its content of cemented metal and zinc; on this basis, calculations were made of the amount of cemented metal which had transferred to the amalgam, and also of the percentage efficiency of the zinc (the amount of zinc consumed).

In some experiments (Series a) measurement of the potential during cementation was carried out by means of the usual compensation method. For this purpose the apparatus shown in Fig. 1 was used. The reference electrode was a saturated calomel electrode.

On the basis of the ratios of the half-wave potentials of the metals subjected to reduction from their simple and complex salts, to the potentials of the zinc amalgam it is possible to predict that copper, cadmium, lead, and antimony will be cemented from any solution, nickel only from ammonia solution, while iron will not be cemented at all by zinc amalgam.

Experimental results (Table 1) showed that copper, cadmium, and antimony are actually cemented from any solutions; nickel is cemented only when ammonia is used as supporting electrolyte, and iron is not cemented. Lead, despite expectations, is not cemented from sulfuric acid through the potential of lead, calculated on the basis of the solubility product of lead sulfate ($2 \cdot 10^{-8}$), proves to be more positive than the potential of the zinc amalgam. This divergence between theoretical assumptions and practice can apparently be explained by the low rate of the process of solution of lead sulfate.

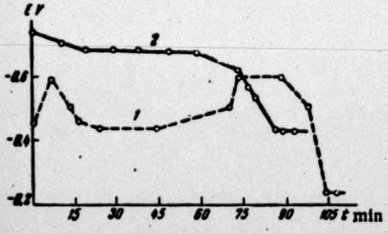


Fig. 2. Change in potential of the amalgam during cementation of lead and cadmium:
1) for Pb; 2) for Cd.

It was noted that during cementation of copper, nickel, lead, and cadmium in solutions of ammonia of low concentrations, black precipitates are formed, while drops of broken up amalgam loose their capacity to fuse into each other. These precipitates, according to spectrographic analysis, contain the reduced metals and finely broken up mercury. With increasing ammonia concentration, the amount of black precipitate decreases. This observation can be explained as follows: at low ammonia concentrations the potential of the amalgam becomes more positive. With the shift in potential to more positive values, the surface tension of the mercury increases, thanks to which, penetration of the metals into the mercury becomes more difficult. For the same reason zinc only dissolves in mercury with difficulty in the absence of electrolyte. The presence of any electrolyte shifts the potential of the amalgam to more negative values, and at the same time depresses the surface tension of the mercury.

TABLE 1

Cementation of Metals by Zinc Amalgam in Various Media

Concentration of Zn in the amalgam in %	Metal	Supporting electrolyte				Observations
		0.1 M HCl	0.1 M H_2SO_4	0.1 M NH_4OH	1 M NH_4OH	
2	Cu	+	+	+	+	With increasing ammonia concentration, the amount of metal passing into the amalgam increases
3	»	+	+	+	+	
5	»	+	+	+	+	
2	Cd	+	⊕	0	0	
3	»	⊕	⊕	0	0	
5	»	⊕	⊕	0	0	
2	Pb	⊕	—	0	0	
3	»	⊕	—	0	0	
7	»	⊕	—	0	0	
2	Ni	—	—	~	~	
3	»	—	—	~	~	
3	Sb	Δ	Δ	Δ	Δ	

Arbitrary Designations: ⊕) Metal is cemented in equivalent amounts with respect to zinc; +) cementation with formation of intermetallic compound; 0) cemented in equivalent amounts, but does not transfer quantitatively into the amalgam; Δ) cemented without formation of amalgam; ~) cemented, but not in equivalent amounts and does not transfer quantitatively into the amalgam.

TABLE 2

Cementation of Copper by Zinc Amalgam

Concentration of Supporting Electrolyte 0.1 M/Liter; Amount of Amalgam 100 g

Electrolyte	Concentration of Zn in the amalgam in %	Amount of Cu in g in the solution before commencement of cementation	Amount of Cu in g remaining in solution after cementation	Amount of Zn in g which goes into solution during cementation	Amount of Cu in g which goes into the amalgam	Amount of Zn in g remaining in the amalgam	Potential at the beginning of the process	Potential of the amalgam at the end of the process	Atomic relation of zinc and copper in the amalgam	Time spent on cementation after drop in potential (in hours)
HCl	1	2.2905	1.9665	0.3486	0.3240	0.6514	—0.74	+0.21	2 : 1	—
HCl	1	2.3095	1.8954	0.4727	0.4642	0.5273	—0,74	+0.21	1.1 : 1	1
HCl	1	2.3095	—	—	—	—	—0.74	+0.31	1 : 1	—
HCl	2	2.3095	1.6680	0.6316	0.6415	1,3580	—0.74	+0.21	2,01 : 1	—
HCl	2	2.3095	1.4092	0.8796	0.9003	1.1204	—0.74	+0.21	1.2 : 1	15
HCl	2	2.3095	1.3435	0.9956	0.9660	1.0440	—0.74	+0.31	1 : 1	—
HCl	2	2.3095	1.2034	1.1842	1.0872	1.1842	—0.74	+0.31	0.72 : 1	11
HCl	4	2.3095	1,0646	1,2685	1.2449	2.7315	—0.85	+0.21	2 : 1	—
HCl	5	2.3095	0.7224	1,5883	1.5871	3.417	—0.77	+0,21	2 : 1	—
NH_4OH	2	2,2905	1.7210	0.7100	0.6790	1.2900	—0.91	—0.08	1,9 : 1	—
NH_4OH	2	2,2905	1.4493	0.9686	0.7712	1.0314	—0.89	—0.16	1.3 : 1	13
NH_4OH	2	2.405	1.5130	1.2107	0.8870	0.7893	—0.91	—0.01	0.87 : 1	3 min.
NaOH	2	2,2905	1.6300	0.6818	0.6605	1.3182	—1.19	—0.55	1.94 : 1	—
NaOH	2	2,2905	1.3855	0.9337	0.9055	1.0663	—1.19	—0.25	1 : 1	—

Measurements of the potentials of the amalgam during cementation in hydrochloric acid solutions show that, in the case of cadmium (Fig. 3, Curve 2), the potential of the amalgam changes from the potential of zinc (at the start of the process) to that of cadmium (at the end of the process). The amount of cadmium reduced is equivalent to the amount of zinc. The change in potential of the amalgam is shown in Fig. 2 (Curve 1). Lead is also cemented in amounts equivalent to those of zinc.

We suggest that the variations in potential of the amalgam, which can be seen in the curve, are determined by the formation of a film of metallic lead on the amalgam surface: the rate at which lead dissolved is less than its cementation rate. In the case of copper, here the chemical interaction between copper and zinc in the amalgam obviously affects the character of the cementation process. During a certain time interval (in 0.1 M HCl) the amalgam potential corresponds to the zinc potential, while it subsequently changes rapidly to + 0.21 V (Fig. 3, Curve 1). On using a more concentrated amalgam (4-5%) instead of the 2% amalgam, the same effect is observed, but with the difference that the potential jump occurs after a longer time interval, and the horizontal section of the curve increases. The potential jump to +0.21 occurs when there is still an appreciable amount of zinc left in the amalgam. By means of quantitative analysis we calculated the ratio of zinc to copper in the amalgam at the point where there is a sudden drop in potential. This ratio proved to be 2:1 (independently of the concentrations of the amalgam used). This seems to suggest formation of a compound with the composition Zn_2Cu in the amalgam.

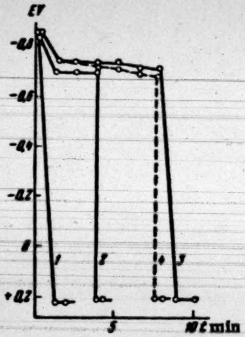


Fig. 3. Change in the potential of the amalgam during cementation of copper; 1) 1% amalgam; 2) 2% amalgam; 3) 3% amalgam; 4) 5% amalgam.

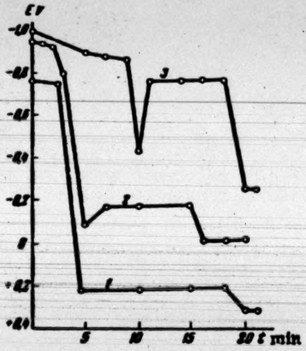


Fig. 4. Change in the potential of the amalgam during cementation of copper in various media: 1) 0.1 M HCl; 2) 0.1 M NH_4OH; 3) 0.1 M NaOH.

A compound of the composition indicated has actually been found by Pushin [10], in copper-zinc alloys. Russel [11], detected it in amalgams using a totally different method – oxidation of amalgams with chemical reagents ($KMnO_4$ etc).

After the occurrence of the first potential jump, formation of a precipitate of cuprous chloride starts in solution. Subsequently, after a certain time interval, there is observed a second jump to +0.31 V (Fig. 4, Curve 1). The ratio of zinc to copper in the amalgam corresponding to this potential jump proved to be 1:1, which suggests the formation of a second compound of copper and zinc with the composition ZnCu. We suggest that the compound Zn_2Cu dissociates according to the equation:

$$Zn_2Cu \rightleftharpoons ZnCu + Zn,$$

while the zinc formed as a result of this dissociation, immediately reacts as follows: $Zn + 2Cu^{2+} \rightleftharpoons Zn^{2+} + 2Cu^{+}$.

Further, metallic copper is formed according to the equation: $2Cu^+ \longrightarrow Cu + Cu^{2+}$, this copper then goes into the amalgam and reacts with the compound found in the amalgam as follows:

$$Zn_2Cu + Cu \rightleftharpoons 2ZnCu$$

On further agitation, the reduction of copper by the zinc separating out from the compound does not stop either.

TABLE 3

Effect of Concentration of Supporting Electrolyte on the Rate of Cementation of Metals by Zinc Amalgam

Supporting electrolyte in M/liter		Metal	Amount			% Efficiency of zinc (i.e. amount usefully employed)
			Me, separated after 15 minutes	Zn used up in extracting the metal	Zn used for evolution of hydrogen	
HCl	0.01	Cu	0.032	0.032	0.006	84
	0.1		0.036	0.037	0.006	86
	1		0.037	0.039	0.009	79
H_2SO_4	0.01		0.035	0.036	0.006	86
	0.1		0.035	0.036	0.009	80
	1		0,035	0.036	0.011	77
NH_4OH	0.01		0,005	0.005	0.015	25
	0.1		0,040	0.0308	0.0132	70
	1		0.038	0,0387	0,0063	86
HCl	0.01	Cd	0.023	0.013	—	100
	0.1		0,025	0.013	—	100
	1		0.030	0,017	—	100
H_2SO_4	0.01		0.023	0.013	—	100
	0.1		0.025	0.013	—	100
	1		0.030	0,017	—	100
NH_4OH	0.01		0.005	0.003	0.001	75
	0.1		0.016	0.009	0.001	90
	1		0.022	0.013	—	100
HCl	0.01	Pb	0.034	0.011	0,005	68
	0.1		0.035	0,011	0.006	65
	1		0.030	0,0094	0.0086	52
NH_4OH	0.01		0.008	0.0025	0.0025	50
	0,1		0.027	0,0085	0.0015	85
	1		0.017	0,0053	0.0047	53
HCl	0.01	Sb	0.031	0,017	0.032	34
	0.1		0.036	0,019	0.090	18
	1		0.035	0,019	0.226	7
H_2SO_4	0.01		0.024	0,013	0.020	40
	0.1		0,036	0,019	0.120	14
	1		0,026	0.012	0.168	6
NH_4OH	0.01	Ni	Traces	—	—	—
	0,1		0.023	0,025	0.003	89
	1		0.035	0,039	—	100

Experiments carried out in 0.1 N ammonia and alkali solutions respectively, showed (curves 2, 3, Fig. 4), that during cementation of copper under these conditions, two potential jumps are observed:

	Alkali supporting electrolyte	Ammonia supporting electrolyte
First jump	−0.55 V	−0.08 V
Second jump	−0.25 V	−0.01 V

In this case, after the first potential jump, there is a new shift to a negative value (this was not observed in hydrochloric acid media).

The ratio of copper to zinc corresponding to the first jump is 2 : 1, while for the second jump the ratio is 1 : 1. In alkali media, after the first jump, a precipitate of Cu_2O is formed, while in the ammoniacal media, the precipitate of Cu_2O dissolves to form the complex $(Cu/NH_3/_2)_2SO_4$.

By means of such investigational methods as anodic oxidation of amalgams, polarographic methods, titration of amalgam with mercury salts, we could not establish the presence of a copper-zinc compound with a zinc content greater than 50% (in terms of number of atoms) in the amalgam. It follows therefore that the cementation method, together with measurement of potential, may give a more complete picture of the chemical interactions between cemented and cementing metals in an amalgam.

The second series of experiments, as indicated above, were devoted to finding out the effect of electrolyte concentration on the rate of cementation and on the amount of zinc usefully employed. Results are given in Table 3.

The results obtained indicate that the nature and concentration of electrolyte has an effect both on the rate of the cementation process, and on the amount of zinc usefully employed. The process rate in acid solutions, exceeds, as a rule, the rate in ammonia solutions. Increasing the supporting electrolyte concentration speeds up the cementation process; this is the result of an increase in the electrical conductivity of the solution, and an increase in current of the local elements which follows from this.

The amount of zinc usefully employed decreases as the electrolyte concentration increases. An exception in this connection is cadmium, which it is known has a high hydrogen overvoltage. There is a particularly sharp drop in the percentage of zinc usefully employed in the case of antimony cementation.

SUMMARY

1. It has been demonstrated that it is possible to use zinc amalgam for the quantitative extraction of cadmium and antimony from hydrochloric, sulfuric, and ammonia solutions; lead – from hydrochloric and ammonia solutions; and nickel – from ammonia solutions, with subsequent formation of amalgam (exception Sb).

2. It has been established that for equivalent ratios of zinc in the amalgam and copper in solution, copper is not quantitatively extracted from solution by a zinc amalgam, because of the formation of chemical compounds Zn_2Cu and ZnCu. Definite potential jumps were found to correspond to the formation of the compounds indicated. Quantitative extraction of copper can be achieved by using a zinc amalgam, containing zinc in amounts which exceed the copper content of the solution by not less than 3 times this amount.

3. It has been shown that measurement of the potential of the amalgam cementation permits one to establish the presence of chemical compounds of the cemented and cementing metals respectively, in the amalgam at the moment when they are formed; this may prove to be an effective method for studying amalgams.

4. The effect of electrolyte concentration on the rate of the cementation process, and on the amount of zinc usefully employed has been studied.

Received June 30, 1954

LITERATURE CITED

[1] H. Hohn, Öster. Chem.-Z., 49, pp. 15-31 (1948).

[2] V. D. Ponamarev and S. M. Gubelbank, J. Gen. Chem., 9, 1365 (1939).

[3] V. D. Ponomarev, J. Appl. Chem., 17, 151 (1944).

[4] V. D. Ponomarev, J. Gen. Chem., 11, 1207 (1941).

[5] Ten Josii, C. A., 35, 405 (1941).

[6] Someya Kin-Ichi, C. A., I, 2346, II 1182 (1927).

[7] N. A. Tananaev, "Volumetric Analysis", State Gen. Sci. Tech. Press (1939).

[8] M. I. Kozlovsky, S. P. Bukhman, and A. T. Malyuk, Trans. Commiss. on Analytical Chemistry, Vol. IV (VII), 1952, p. 263.

[9] M. I. Kozlovsky and S. P. Bukhman, Bull. Acad. Sci. Kazakh SSR, Chem. Series, No. 4 (1951).

[10] N. A. Pushin, J. Russ. Phys. Chem. Soc., 28, 659 (1906).

[11] A. S. Russel et al., J.Chem. Soc., pp. 837-841 (1932.

BLANK
PAGE

A MERCURIMETRIC METHOD OF DETERMINING IODIDES

R. Kh. Zamanov

I. P. Pavlov Samarkand Medicinal Institute

On addition of mercuric salts to an excess of iodide solution the complex ion HgI_4^{2-} is formed. On addition of more Hg^{2+} ions, as a result of the reaction

$$HgI_4^{2-} + Hg^{2+} \rightarrow 2HgI_2,$$

near the equivalence point, a yellow turbidity of HgI_2 appears, on shaking, the color changes to red. This reaction was first used for quantitative determination of iodides in 1832 by Morozeau [1]. Nevertheless, because of the necessity of introducing corrections for the appearance of the red turbidity before the equivalence point, the method has not been widely used. Stanek and Nemes [2], titrated iodides in the presence of sodium nitroprusside which forms a turbidity with the Hg^{2+} ion at the equivalence point. Practice has shown that when sodium nitroprusside is used as the indicator, it is not possible to determine more than 20 mg of iodide in 200 ml of solution being titrated; otherwise the turbidity of HgI_2 which appears does not permit the titration end-point to be established.

Dubsky and Trtilek's method [3], is a more convenient mercurimetric method for determining low concentrations of iodides; they suggested titrating the test iodide solution with mercuric nitrate in an acid medium, in the presence of diphenylcarbazone which forms with Hg^{2+} a violet colored compound. Just as in the previous instance, however, titration of more concentrated iodide solution is rather difficult on account of precipitation of HgI_2 at the end-point. In order to increase the sensitivity of the indicator change, the authors were compelled to titrate in a standard flask until the appearance of a color which indicates that the reaction is coming rapidly to an end; at this point they added water, made the solution up to the mark, and filtered off the precipitate of HgI_2 formed; subsequently a known volume of the solution in the standard flask was titrated until the appearance of a red-violet color. It is quite understandable why Dubsky and Trtilek's method, despite the high sensitivity of the indicator, has not found wide practical application; it is the result of the complexity of operations and the difficulty in finding the end-point. The basic factor which complicates carrying out titration, in the given instance, is the appearance of the HgI_2 precipitate. This drawback can be eliminated by replacing water – the usual solvent – by another liquid in which the HgI_2 formed during the reaction is soluble. Experiments which we carried out showed that ethyl alcohol is capable of dissolving enough of the HgI_2; in addition, use of this solvent leads to an increase in sharpness of indicator change and enhances the sensitivity.

In order to determine the optimum titration conditions for iodides in an aqueous-alcohol medium, we titrated 0.01 N solution of potassium iodide with a solution of $Hg(NO_3)_2$ of roughly the same concentration in solvent mixtures containing different amounts of alcohol, and which are slightly acidified with nitric acid. A 1% alcohol solution of diphenylcarbazone was used as indicator. Results are given in Table 1.

Accordingly, the most suitable medium for working with 0.01 N solutions proved to be an aqueous alcohol one, consisting of 5 ml of 96° alcohol and 1 ml of test iodide solution. Under these conditions, the solution remains perfectly clear up to the end point, while the color change of the indicator is exceptionally sharp. Titration of iodides in a homogeneous medium does not require the introduction of any corrections.

TABLE 1

Mercurimetric Titration of KI (1.243 mg I^-/ml) in Aqueous and Aqueous-Alcohol Media

Volume in ml		Amount of ~0.01 N $Hg(NO_3)_2$ used in ml	I^- found in mg	Error in %	Observations
Water	Alcohol				
5.0	0.0	1.140	1.236	−0.56	Lots of precipitate formed
4.0	1.0	1.140	1.236	−0.56	Indicator color change not sharp enough
3.0	2.0	1.140	1.236	−0.56	
2.0	3.0	1.142	1.238	0.40	Turbidity appears towards end of titration
0.0	5.0	1.146	1.243	0.00	Solution remains clear up to the end-point. Color change at end-point exceptionally sharp.

TABLE 2

Mercurimetric Determination of Small Amounts of I^- Ions in a Homogeneous Aqueous-Alcohol Medium

I taken in mg	I found in mg	Error in %	I taken in mg	I found in mg	Error in %
0.870	0.8706	+0.07	1.612	1.612	0.00
1.243	1.243	0.00	1.740	1.737	−0.11
1.491	1.491	0.00	1.864	1.859	−0.26
1.368	1.372	+0.29			

The following solutions are necessary for iodide determination: 1) 0.01 N $Hg(NO_3)_2$; 2) 1% alcohol solution of diphenylcarbazone (stable for weeks); 3) approximately 1 N HNO_3.

Standard $Hg(NO_3)_2$ of the concentration indicated is prepared from chemically pure mercuric oxide; for this purpose 1.09 g of HgO is moistened in a liter standard flask with a small amount of water, it is dissolved by addition of 1.5-2.0 ml of concentrated nitric acid. When the precipitate has dissolved completely the solution is made up to a liter with water and filtered. In the absence of mercuric oxide, the $Hg(NO_3)_2$ solution can be prepared by dissolving metallic mercury in HNO_3 [4].

The standard mercuric nitrate solution was standardized against 0.01 N KCl. For this purpose, to one 1 ml of KCl solution is added 5 ml of 96° alcohol free of halides, and two drops of the 1% alcoholic solution of diphenylcarbazone; the solution is acidified with one or two drops of 1 N HNO_3 until the color which is formed on addition of the indicator disappears, and the whole titrated with $Hg(NO_3)_2$ from a micro-buret to the appearance of a weak violet-rose color.

Determination of iodide is carried out in excatly the same way as standardization of 0.01 N $Hg(NO_3)_2$. To 1 ml of test liquid containing approximately 0.13-0.15 g of iodide in 100 ml of solution is added 5.0 ml of 96° alcohol, 2 drops of the 1% alcoholic solution of diphenylcarbazone, 1-2 drops of nitric acid and the whole titrated with 0.01 $Hg(NO_3)_2$ to the appearance of a weak violet-rose color.

Table 3 contains some results for the determination of iodide in chemically pure preparations of lead iodide and potassium iodide.

In addition to studying the conditions for titrating iodides in dilute solution, we were also interested in the possibility of working with 0.1 N solutions. Experiments which we carried out showed that on addition of sufficient alcohol to the amount of working solution taken, such a method can be realized. Optimum conditions are achieved in such cases by adding to 1.0 ml of 0.1 N test solution, 10 ml of ethyl alcohol. When such a ratio of

TABLE 3

Test compound	Weight taken in mg	I content in %		Error in %
		Found	Theoretical	
PbI_2	0.3141	55.22	55.05	+0.17
PbI_2	0.3141	55.22	55.05	+0.17
KI	1.6260	76.35	76.45	−0.10
KI	1.6260	76.50	76.45	+0.08

the volume of solution to be titrated and alcohol (1 : 10) is used, the working solution remained clear to the endpoint, and the indicator color change is exceptionally sharp.

For the determination of iodide in potassium iodide, 0.980 ml of 0.1 N $Hg(NO_3)_2$ was used to titrate 1.0 ml of solution to be titrated containing 16.257 mg of iodide; this corresponded to 76.47% I (theoretical content 76.45%). For titration we used, in all cases, a tapless pneumatic micro-buret, since we preferred this type to all other models of similar apparatus.

It should be pointed out in conclusion, that apart from its advantages over other mercurimetric methods proposed previously, this method can compete in accuracy with iodometric methods, since the sensitivity of diphenylcarbazone in alcohol media towards Hg^{2+} ions is several times higher than that of the iodine-starch reaction.

SUMMARY

A simple and convenient mercurimetric method has been developed for the determination of iodides by titration in aqueous-alcohol media. The method does not require any corrections and is distinguished by a high accuracy.

Received November 12, 1954

LITERATURE CITED

[1] Morozeau, J. pharm. chim. 18, 302 (1832).

[2] Vl. Stanek, T. Nemes, Chem. Obzor. 8, 21 (1933); Vgl. 8, 41 (1933), cited by I. V. Dubsky and J. Trtilek, Mikrochemie, 15, pp. 95-98 (1934).

[3] I. Dubsky and J. Trtilek, Mikrochemie, 15, pp. 95-98 (1934).

[4] I. M. Mavlyanov, J. Appl. Chem. 10, No. 12, pp. 2162-2166 (1937).

BLANK
PAGE

A METHOD OF CONCENTRATING TRACES OF COPPER BY MEANS OF ORGANIC REAGENTS

V. T. Chuiko and A. U. Mamenko

Cherkassk Teacher's Training College

We have shown [1], that quantitative concentration of traces of a metal (micro component) by partial precipitation of another metal (macro-component) as a basic salt, can only be achieved under such conditions that a known amount of the latter is precipitated; under these conditions, with changes in concentration of the micro-component metal, all other conditions being equal, the micro-component will be distributed between solution and precipitate in a constant ratio. It was also noted that during concentration of the method considered, practically complete separation of impurities, in the form of those metals which form more soluble compounds with the reagent than the macro-component metal, can be effected [2].

When 8-hydroxyquinoline which forms inner-complex compounds with metals is used as a reagent, different regularities were observed. If, for sufficiently high concentrations of the micro-component metal, the latter practically completely goes over into the precipitate, then on decreasing the concentration to a known limit, the amount of it which is caught in the precipitate will decrease sharply (Table 1). In addition, it was established that at a concentration of the micro-component near to this limit, the amount of it trapped in the precipitate decreases with increasing solution volume, and hardly changes at all with increasing macro-component concentration. In this connection, it was of interest to establish: a) the effect of a subsequent extraction of precipitate with a non-miscible solvent (after precipitation of part of the macro-component with an organic reagent) and b) the possibility of separating, during concentration in this way, impurities in the form of metals which form more soluble compounds (or less stable complexes) with the organic reagent than the macro-component metal does.

For solving the first problem we used 8-hydroxyquinoline as reagent, while for solving the second we used – diethyldithiocarbamate.

1. Concentration of Copper from a Solution of Lead Nitrate by Means of 8-Hydroxyquinoline

Investigation of concentration by means of 8-hydroxyquinoline was carried out as follows: to 8 ml of 0.1 M lead nitrate, purified from copper by precipitation with hydrogen sulfide [2], was added a solution of a copper salt, 1 ml of 2 M sodium acetate and 0.5 ml of 0.15 M 8-hydroxyquinoline solution (quinosol). The mixture was shaken for 5 minutes and then centrifuged, the precipitate was washed with 5 ml of distilled water and dissolved in 2 ml of 2N nitric acid. Copper was then determined in the solution thus obtained after adding sulfuric acid to it and making its volume up to 10-12 ml, by the dithizone method (by the method of mixed colors [3]). A blank run in exactly the same way, was used as a standard; in this case, copper was introduced into the nitric acid solution obtained after dissolving lead 8-hydroxyquinolate.

Using the same conditions, parallel experiments were carried out on concentration of copper by partial precipitation of lead as the 8-hydroxyquinolate, with subsequent extraction of the precipitate with chloroform. The 8-hydroxyquinolates were extracted with 5-6 lots of 3 ml of chloroform; after this, the lead and copper were transferred to the aqueous layer by shaking up with 2 lots of 2 ml of nitric acid; copper was extracted from the latter with dithizone.

TABLE 1

Copper introduced in γ	Copper found in the precipitate in %	Copper found in the chloroform layer in %
50	98	–
40	95	–
30	97	–
20	67	99
10	34	100
5	24	105

Results of these tests are given in Table 1.

As can be seen from Table 1, with decreasing copper concentration, starting at 30 γ in 10 ml, the amount of it trapped in the precipitate decreases sharply. If the precipitate which forms after partial precipitation of the lead is extracted with chloroform, the copper goes over completely into the chloroform layer. This fact is in complete agreement with the thesis advanced by Babko [4]; according to Babko, during extraction of reaction products with a non-miscible solvent, equilibrium is displaced toward formation of the final product.

2. Concentration of Copper from Cadmium and Lead Salt Solutions by Means of Diethyldithiocarbamate

Diethyldithiocarbamate forms colorless or colored precipitates with a number of metals [5]; we were unable to find any data on the solubility of these precipitates in the literature. Accordingly, in choosing mixtures of metal salts which would be suitable for our purpose, we followed Kuznetsov's precepts [6], according to which a parallelism can be observed between reactions with organic and inorganic reagents possessing similar functional groups. In the case of diethyldithiocarbamate, it may be postulated that it forms with metals, compounds whose solubility in water changes in the same order as the sulfides. On the basis of these considerations, we choose cadmium and lead as macro-components. Copper was the micro-component, while the impurities consisted of metals which are normally present in cadmium and lead as contamination, and form colored compounds with diethyldithiocarbamate.

a) Determination of Copper in Cadmium Salts. Technical requirements specify determination of lead, zinc, iron, and copper in cadmium; of these, lead and zinc, like cadmium itself, form white precipitates with diethyldithiocarbamate. Thus, in developing a diethyldithiocarbamate method for determining copper in cadmium it was only necessary to determine the effect of iron; nevertheless, in a number of tests, we also added 2 mg each of lead and zinc, which, as was shown, did not affect copper determination.

The solution of cadmium chloride used for the tests, was freed from copper by extraction of the latter as the diethyldithiocarbamate with chloroform. Solutions of iron, lead, and zinc salts were purified by partial precipitation as sulfides.

Experiments on copper determination were carried out as follows: to the cadmium chloride solution was added solutions of copper, and iron, 1 ml 1 N nitric acid and 2 ml of 0.1% sodium diethyldithiocarbamate, after which copper was extracted with 2 lots of 2 ml chloroform. A standard was prepared by extracting copper from an aqueous solution acidified with nitric acid. Comparison of the colors were carried out in the chloroform layer in a visual colorimeter.

Results are given in Table 2.

On the basis of the results given in Table 2, it is possible to conclude that copper as the diethyldithiocarbamate can be quantitatively extracted from a solution of a cadmium salt, and that iron does not interfere with copper determination at iron contents of up to 0.05 mg.

b) Determination of Copper in Lead Salts. Of the metals which form colored precipitates with diethyldithiocarbamate, bismuth, iron, nickel, and cobalt, as well as copper, can be present as impurities in lead. Lead itself forms a white precipitate with this reagent.

Experiments were carried out in exactly the same way as for determination of copper in cadmium salts, using solutions of the metal salts (analytical grade) purified by partial precipitation with hydrogen sulfide. Results of these experiments showed that contamination by bismuth, iron, nickel, and cobalt in amounts permitted by All-Union Standards for Analytical Grade lead nitrate does not prevent determination of copper down to

TABLE 2

Amount of 1 M Cadmium chloride taken in ml	Copper added in γ	Iron added in mg	Copper found in %
3	5	–	100
3	10	–	98
10	10	–	102
20	10	–	98
10	10	0.05	100
10	10	0,1	105
3	10	0.2	135

0.0001%[*]. With increasing amount of impurities up to the limits shown in Table 3, bismuth and iron were observed to shift over into the chloroform layer, as a result, the results obtained were on the high side. Nevertheless, even in these cases, satisfactory results were obtained, under conditions where the standard was prepared by extracting copper from test solution, after extracting the copper to be determined from it, (see below).

c) Determination of Copper in Nickel and Cobalt Salts. Results of tests given in Table 3, led us to think that lead ions may act as a regulator of the concentration of free diethyldithiocarbamate during extraction of copper from nickel (cobalt) salts also. Nevertheless, tests showed that on increasing the amounts of nickel and cobalt to more than 0.1 mg in 10 ml of lead nitrate solution, they start to be extracted in appreciable amounts by the chloroform and impart a color to the latter. In addition, even for an amount of nickel of 1 g, only ~83% of the copper goes over into the chloroform layer[**].

TABLE 3

Amount of 1 M Lead Nitrate taken in ml	Copper added in γ	Amount of impurities added in mg	Copper found in %
20	10	—	99
20	5	—	100
10	10	0.10 Bi	100
10	10	0.25 Bi	115
10	10	1.0 Ni	96
10	10	1.0 Co	100
10	10	0.1 Fe	100
10	10	0.5 Fe	105
10	10	0,1 Ni. Co. Fe & 0.01 Bi	100
10	10	0.1 Ni, Co. Fe & 0.05 Bi	115

Complications connected with the transfer of some of the nickel (cobalt) into the chloroform layer, and the incomplete extraction of copper, where overcome as follows: errors were compensated for, by preparing a standard by extracting a known amount of copper from test solution after extracting the copper to be determined from it. Under these conditions, both nickel (cobalt) and copper were distributed between the solvents in equal proportions. As a result, the color of the chloroform extract of test solution and that of the standard solution will be weakened to an equal extent, because of incomplete extraction of copper, while they will be strengthened to an equal extent because of extraction of some of the nickel (cobalt).

Copper was determined in nickel (cobalt) nitrate as follows: to 10 ml of 1 M lead nitrate was added a known amount of copper and nickel (cobalt) solutions, followed by 1 ml of 1 N nitric acid an an exactly measured volume (4 ml) of 0.1% sodium diethyldithiocarbamate solution, after which copper was extracted with two lots of 2 mls of chloroform. A standard was prepared by adding copper to the aqueous solution left after removal of the copper to be determined, followed by addition of 2 ml of diethyldithiocarbamate solution; subsequent procedure was the same as for the first extraction[***]. Comparison of the colors of the chloroform solutions, as in previous

---

[*] We did not try to determine smaller amounts of copper.

[**] We determined the amount of copper extracted by the chloroform by comparing the color of the chloroform solution obtained by extracting copper from 10 ml of 1 M lead nitrate and 1 g of nickel, with the color of the united extracts, copper – from an aqueous solution, and nickel – from a solution of lead nitrate.

[***] For amounts of nickel (cobalt) greater than 0.3-0.4 g, some products of a yellow-brown color were extracted by the chloroform, the colors produced by these compounds disappeared after 10-15 minutes.

TABLE 4

Amount of nickel (cobalt) taken in g	Copper added in γ	Copper found in %
0.05 Ni	10	100
0.1 Ni	10	95
0.2 Ni	10	97
1.0 Ni	10	100
0.025 Co	10	100
0.1 Co	10	97
1.0 Co	10	96

instances, were carried out in a visual colorimeter. It would be better however, in the given instance, to carry out colorimetric measurements in a photocolorimeter).

Results on the determination of copper in nickel and cobalt salts by the method suggested, as can be seen from Table 4, are completely satisfactory. One whould bear in mind however, that the change in color with change in copper concentration does not strictly follow Beer's law, since a constant light absorption determined by nickel (cobalt) is superimposed on the light absorption of copper diethyldithiocarbamate. Moreover, on the same principle, accuracy of colorimetric determination will also decrease with decreasing copper amounts in the test sample (according to our observations, satisfactory results can still be obtained for 10 γ copper in the test).

SUMMARY

1. Using concentration of copper from a solution of a lead salt by partial precipitation of the latter as an example, it has been shown, using 8-hydroxyquinoline as reagent, that copper is quantitatively trapped in the precipitate only when its concentration reaches a certain limit. With a decrease in copper concentration below this limit, the extent to which it is trapped in the precipitate decreases rapidly.

Quantitative removal of copper from the solution of a lead salt in this last instance, may be achieved by extracting the precipitate with a non-miscible solvent.

2. It has been shown that chloroform extraction of traces of copper as diethyldithiocarbamate from aqueous lead nitrate solutions, prevents extraction of bismuth, iron, nickel, and cobalt present as impurities, but does not prevent quantitative separation of copper. Cadmium chloride behaves similarily during extraction of copper from a solution containing iron as impurity.

On the basis of this action of the salts of lead and cadmium, methods have been developed for determining traces of copper in salts of lead, cadmium, nickel, and cobalt.

Received August 6, 1954

LITERATURE CITED

[1] V. T. Chuiko, Factory Lab., 18, 403 (1952).

[2] V. T. Chuiko, Factory Lab., 17, 146 (1951).

[3] E. B. Sandell, "Colorimetric Determination of Metal Traces", 1949, p. 309.

[4] A. K. Babko, Factory Lab., 11, 999 (1945).

[5] Yu. A. Chernikhov and B. M. Dobkina, Factory Lab., 15, 906 (1949).

[6] V. I. Kuznetsov, J. Anal. Chem., 2, 67 (1947).

THE PRECIPITABILITY OF STRONTIUM OXALATE IN THE PRESENCE OF OTHER IONS

M. P. Babkin

Donetzk Industrial Institute

In order to precipitate strontium completely as the oxalate, it is recommended that this salt be precipitated from an aqueous-alcohol solution using a definite excess of the precipitant — oxalic acid or ammonium oxalate [1, 2]. Since the solubility of strontium oxalate is relatively high in water — $2.3 \cdot 10^{-4}$ mol/liter [3], it is recommended also that the precipitate be washed with a saturated solution of strontium oxalate in order to cut down losses [4]. The presence in solution of salts which have a common ion with the precipitate, usually, increases its solubility and thereby decreases the amount precipitated. According to Pochinok's results [5], the solubility of strontium oxalate in 0.025 N ammonium chloride is 0.0957 g/liter, or $5.5 \cdot 10^{-4}$ mol/liter, while in 0.033 N ammonium chloride the corresponding figures are 0.1052 g/liter or $6.0 \cdot 10^{-4}$ mol/liter, i.e., 2.4-2.6 times its solubility in pure water.

In the present article we present results of experiments carried out to establish the effect of the presence in aqueous solution of potassium nitrate, potassium chloride, and ammonium acetate in various amounts on the precipitability and solubility of strontium oxalate, when equivalent amounts of strontium nitrate and ammonium oxalate are used and also when excess of the latter is used.

1. The Precipitability of Strontium Oxalate on Pouring Together Equivalent Amounts of Strontium Nitrate and Ammonium Oxalate

To 50 ml of a 0.01 N solution of ammonium oxalate was added a known amount of dry potassium nitrate, potassium chloride, or ammonium acetate; the solution was heated to the boil and 25 ml of a 0.02 N solution of strontium nitrate added to it. The concentration of the mixed salts at the moment when they were poured together was 0.0033 mol/liter. After 2 days the precipitate of strontium oxalate was filtered off, washed with cold water (~ 25 ml), dissolved in sulfuric acid and titrimetrically determined with 0.01 N potassium permanganate. Precipitability in the control test (in the absence of other salts) was taken as 100%. The solubility of strontium oxalate in mol/liter was calculated by means of the formula

$$\frac{(V_1 - V_2) \cdot K_1 \cdot K_2 \cdot 10^{-3}}{2} + 2.3 \cdot 10^{-4},$$

where V_1 is the volume of $KMnO_4$ in mls used in the control test; V_2 is the volume of $KMnO_4$ in mls used for test solution; K_1 is the normality coefficient of the $KMnO_4$; K_2 the coefficient for converting the volume of filtrate to 1 liter.

The difference $(V_1 - V_2)$ in mls of $KMnO_4$ corresponds to the difference in weight of the strontium oxalate precipitates which separate out from a solution which does not contain a salt with other ions (VI) and from a solution which contains such a salt (V_2), i.e. it corresponds to the amount of SrC_2O_4 which remains unprecipitated, as a result of the action of the salt with other ions. By multiplying this difference by the normality of the $KMnO_4$ (K_1), we get the number of milligram equivalents, while by dividing by two we get the number of millimols of strontium oxalate, remaining under the influence of other salt in solution, the volume of which is composed of the volumes of strontium nitrate and ammonium oxalate poured together and the volume of wash water. This volume amounted to 100 ml (75 ml of solutions poured together + 25 ml of wash water) for the tests whose results are given in Tables 1 and 2. The coefficient (K_2) for converting to a volume of 1 liter is 10. The factor 10^{-3} is

TABLE 1

Precipitability of Strontium Oxalate in the Presence of KNO_3, KCl, and CH_3COONH_4 When Equivalent Amounts of $Sr(NO_3)_2$ and $(NH_4)_2C_2O_4$ (0.0033 mol/liter) are Used

KNO_3, KCl CH_3COONH_4 in mol/liter	Precipitability in %			Solubility in mol/liter		
	KNO_3	KCl	CH_3COONH_4	KNO_3	KCl	CH_3COONH_4
0.0	100.0	100.0	100.0	$2,3\cdot10^{-4}$	$2,3\cdot10^{-4}$	$2.3\cdot10^{-4}$
0.1	84.0	88.7	90.0	$5,6\cdot10^{-4}$	$4,4\cdot10^{-4}$	$4.3\cdot10^{-4}$
0.2	78.7	80.6	75.6	$5,9\cdot10^{-4}$	$5.9\cdot10^{-4}$	$7.1\cdot10^{-4}$
0.4	68.1	67.2	60.0	$8,3\cdot10^{-4}$	$8.3\cdot10^{-4}$	$10.2\cdot10^{-4}$
0.6	59.4	54.6	40.7	$11,1\cdot10^{-4}$	$10,6\cdot10^{-4}$	$14.0\cdot10^{-4}$
0.8	50.0	—	19.5	$13,2\cdot10^{-4}$	—	$18.1\cdot10^{-4}$
1.0	42.2	45.2	7.8	$14,8\cdot10^{-4}$	$12.3\cdot10^{-4}$	$20.4\cdot10^{-4}$

TABLE 2

Precipitability of Strontium Oxalate in the Presence of KCl, NaCl, and Excess $(NH_4)_2C_2O_4$

KCl, NaCl in mol/liter	Excess $(NH_4)_2C_2O_4$ in %	Precipitability in %		Solubility in mol/liter	
		KCl	NaCl	KCl	NaCl
—	—	100.0	100.0	$2.3\cdot10^{-4}$	$2,3\cdot10^{-4}$
0,6	—	52.5	50.4	$13.0\cdot10^{-4}$	$13.1\cdot10^{-4}$
0,6	25	—	64.0	—	$10.2\cdot10^{-4}$
0,6	50	85.6	75.9	$5.5\cdot10^{-4}$	$7.6\cdot10^{-4}$
0,6	100	86.4	89.0	$5.3\cdot10^{-4}$	$4.7\cdot10^{-4}$
0,6	200	89.0	140 0	$4.8\cdot10^{-4}$	—

introduced in order to convert millimols into mols/liter. The solubility of strontium oxalate in pure water ($2.3\cdot10^{-4}$), is added to the value found for the number of mols of strontium oxalate which go into solution under the influence of the other salts present in solution.

Results are given in Table 1.

The precipitability of strontium oxalate in solutions containing potassium nitrate, is somewhat lower than in solutions containing potassium chloride (for equal molar concentrations). For a 1 M concentration of potassium nitrate, precipitability amounted to 42.2%, while for the same concentration for potassium chloride the value was 45.2%. The solubility of strontium oxalate increases 6.4 times in a molar solution of potassium nitrate, and 5.4 times in a molar solution of potassium chloride.

Ammonium acetate depressed the precipitability of strontium oxalate to a significantly greater extent than potassium chloride or nitrate; this can be explained by the fact that, under the precipitation conditions, ammonium acetate hydrolyzes strongly and the ammonia formed during the hydrolysis volatilizes leaving acetic acid, which has a dissolving action on strontium oxalate, to accumulate. In a 1 M solution of ammonium acetate, the precipitability of strontium oxalate falls to 7.8%, while its solubility increases 9 times.

2. Precipitability of Strontium Oxalate in the Presence of Potassium Chloride and Sodium Chloride when Excess Ammonium Oxalate is used.

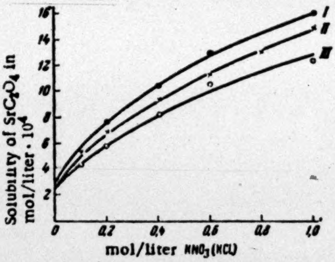
To 50 ml of a 0.01 N solution of ammonium oxalate was added a certain excess of this salt, a known amount of potassium or sodium chloride, and the whole heated to the boil; 25 ml of 0.02 N strontium nitrate was then added. The strontium oxalate precipitate was then determined as usual with permanganate after 2 days. Results are given in Table 2.

The percentage of precipitability of SrC_2O_4 in 0.6 M potassium chloride and sodium chloride, when excess ammonium oxalate is used, increases but even when a 100% excess is used, precipitability still only amounts to 86-89%. For a 200% excess of ammonium oxalate in 0.6 M sodium chloride, a coarse heavy crystalline precipitate formed, the composition of this precipitate, as determined by the volume of $KMnO_4$ required, corresponds to the double salt $(NH_4)_2C_2O_4 \cdot 2.5\ SrC_2O_4$.

TABLE 3

Solubility of Strontium Oxalate in Aqueous Solutions of Potassium Nitrate

KNO_3 in mol/liter	H_2O in ml	Solubility of SrC_2O_4 in mol/liter
—	75	$2.86 \cdot 10^{-4}$
0.2	75	$7.76 \cdot 10^{-4}$
0.6	75	$12.85 \cdot 10^{-4}$
1.0	75	$16.00 \cdot 10^{-4}$



Change in solubility of SrC_2O_4 with salt concentration: I) KNO_3; II) KNO_3 (by precipitation); III) KCl (by precipitation).

3. Solubility of Strontium Oxalate in Aqueous Solutions of Potassium Nitrate

Aliquots of 0.0484 g of $SrC_2O_4 \cdot H_2O$ were placed in beakers containing various weighed amounts of potassium nitrate, 75 ml of water was added, and the mixture left for 7 days with periodic shaking. After 7 days the undissolved strontium oxalate was filtered off, washed and quantitatively estimated with $KMnO_4$ as usual. In parallel, the number of mls of $KMnO_4$ required to oxidize 0.0484 g of $SrC_2O_4 \cdot H_2O$ was determined. Results are given in Table 3.

The solubility of strontium oxalate in distilled water, according to our results ($2.86 \cdot 10^{-4}$ mol/liter), proved to be higher than that given in the literature ($2.3 \cdot 10^{-4}$). It seems possible that the solubility of SrC_2O_4 in water has not yet been exactly determined; e.g., in Kertman's textbook [6], the solubility is stated to be 6.6 g/100 g water, which is equivalent to $660 \cdot 10^{-4}$ g/1000 g water, or $\sim 3.7 \cdot 10^{-4}$ mol/liter.

Results on the solubility of strontium oxalate in potassium nitrate solutions are fairly near the values obtained in experiments on precipitability (Table 1) The solubility of SrC_2O_4 increased 5.6 times in 1 M potassium nitrate. Changes in the solubility of strontium oxalate with concentration of potassium nitrate and potassium chloride are shown in the diagram given above.

SUMMARY

1. The percentage precipitability of strontium oxalate in aqueous solutions containing various concentrations of potassium nitrate, potassium chloride, and ammonium acetate has been determined; the solubility of strontium oxalate in these solutions has been calculated.

2. The effect of excess oxalate ions on the precipitability of SrC_2O_4 from aqueous solutions of potassium chloride and sodium chloride has been studied.

3. The solubility of strontium oxalate in aqueous solutions of potassium nitrate has been determined.

Received October 6, 1954

LITERATURE CITED

[1] G. Leison, Chem. News, 22, 210 (1870).

[2] Peters, Z. Anorg. Chem., 29, 145 (1902).

[3] Yu. Yu. Lurye, "Calculating and Reference Tables", 1947, p. 105.

[4] W. Winkler, Z. angew. Chem., 31, 80 (1918).

[5] Kh. N. Pochinok, J. Appl. Chem., 5, 1078 (1932).

[6] L. Kertman, "Qualitative Chemical Semi-Micro-Analysis", State Chem. Press, Moscow, 1949, p. 393.

SYSTEMATIC AND RANDOM ERRORS IN CHEMICAL ANALYSIS

V. V. Nalimov

The aim of any accurate measurement, including chemical analysis, is not only to get analytical results, but, in addition, to evaluate the reproducibility and correctness of the results obtained. This question has become very pressing at the moment when All-Union State Standards are to be drawn up for spectrographic methods of analysis. When specification tests are being carried out by various methods which differ in principle, it is unavoidable that conflicting results will sometimes be obtained; these conflicts can only be resolved correctly, when reliability limits have been established for each method, in this first instance, of course, for a chemical method. Methods of evaluating errors of reproducibility of chemical analysis are not particularly difficult – in recent years, both abroad, and in Soviet literature [1-4], many papers have appeared which recommend the widespread use of mathematical statistics for this purpose. Evaluation of systematic errors in chemical analysis is however considerably more complex. Usually, standard samples are used for this purpose in the laboratory. Nevertheless, no indications are given in the chemical literature, or in All-Union Standard Methods on chemical analysis, on how to evaluate and standardize systematic errors. In turn, this naturally leads to serious disagreements. Everyday experience shows that, in certain cases, analysis of the same test sample in different laboratories gives essential systematic deviations, despite the fact that, in both laboratories, it has been shown, by replicate analysis of the same standard, that systematic errors are absent. Shaevich [5], has shown that even in the case of analyses carried out with particular care, during preparation of standard samples of casts and steels, systematic deviations were observed between the results of different laboratories. Our work on a study of systematic errors in the chemical analysis of slags has shown that the magnitude of the relative systematic error depends essentially on the chemical composition of test material, and, accordingly, cannot be controlled by means of any one standard sample. There is plenty of evidence at the moment, which indicates that the use of one, or even of several standard samples, is not an effective method for calculating and standardizing systematic errors in chemical analysis. The reason for this is not clear enough. The aim of the present article is to try and clear up this question on the basis of the mathematical theory of errors.

We shall start off by giving a clear definition of the concepts of systematic and random errors. One can only talk about the random error of a chemical analysis when the number of measurements considered are clearly defined and limited. If a variable quantity belonging to this number of measurements, assumes a value which depends on chance, and a distribution function can be determined for it, then such a value can be called a random value [6]. Systematic errors – are errors which arise as a result of one or several definite causes, operating according to certain definite laws [7]. In order therefore to establish the presence of systematic errors, we must know what these laws are [8]; in this case, a systematic error can be regarded as a correction to be applied to the measurements. It is essential to emphasize that the difference between systematic and random errors is very relative – it depends on the number of measurements chosen for consideration, and this choice, by its very nature, is completely arbitrary. For example, if one considers a number of measurements of the diameter of some detail by means of a defective micrometer, then, in relation to this number of measurements, the error introduced by the defect in the micrometer, can be regarded as a systematic error. If then we consider a number of micrometers issued by the factory, the error in the manufacture of the micrometers can be regarded as a random error [9]. Let us take a second example, if we consider a number of measurements carried out at equal temperatures, then with respect to this number of measurements, the error will be a random one. If, then, measurements are carried out at strictly fixed temperatures, and the law is determined which defines how change in temperature affects the results of measurements, the temperature error can be regarded as a systematic one, and even as a correction to be applied to the measurement.

Chemical analysis is a complex measuring process, accordingly, it is necessary to approach the separation of errors into random and systematic errors with particular care. In studying errors of chemical analysis, it is necessary to examine the following numbers of measurements.

1. Let us assume that there is a statistic ensemble consisting of a number of measurements on one standard sample, carried out in one laboratory within a certain time limit. If we take the mean arithmetic value of the analytical results as the center of scatter, then henceforth we shall call the random error obtained with respect to this value, the reproducibility error. Usually, it is quite unjustified to assume that all the random errors of chemical analysis are confined to one reproducibility error. Further, if on carrying out a sufficiently large number of replicate experiments, there is discovered a persistent deviation between the mean value of the analysis and the specified results for the Standard Sample (SS), then we get a constant error, which is usually called the "systematic error" of the chemical analysis, and, it is assumed that it characterizes the systematic error of a chemical analysis as a whole, or at least for test materials, approximating in composition to that of the SS, though the reasons which give rise to this error, and the laws according to which these reasons operate, usually remain unknown. Accordingly, on the basis of the definition given above, this value which is constant for any given number of measurements, cannot yet be considered as the systematic error of the chemical analysis as a whole. In accordance with this division, only errors of reproducibility can normally be the object of the application of mathematical statistics in chemical analysis, since by its very nature, mathematical statistics which is based on the theory of probability, can only deal with random errors. Existing All-Union Standards for chemical analysis also only confine themselves to requirements following from errors of reproducibility, — this follows from the work of Shaevich [5], and also from our own work on the study of errors of reproducibility during analysis of carbon steels*. Thus the large group of errors which have been united without justification under the one term "systematic error", usually remain outside the scope of investigation of the research worker**.

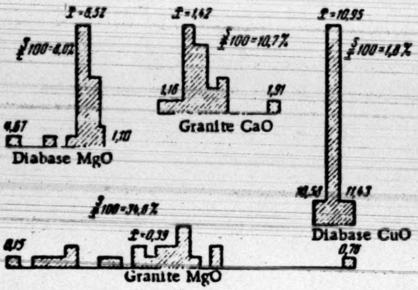


Fig. 1. Histograms for the results of analysis of two silicates according to Fairbairn [10].

2. Let us assume that this same SS be continued to be analyzed in the same laboratory over more or less long time intervals. Now, that value which was formerly constant with respect to the previous number of measurements, becomes a variable quantity. This arises as a result of the fact that a number of factors assumed to be constant during the time the original measurements were made, may later become variables. With time, the purity of the water and the reagents change; the weights suffer from wear; pressure changes, as do humidity, temperature, illumination of the place of work, etc. All these factors, to some extent, will affect the analytical results.

3. Let us also assume that the SS is analyzed in different laboratories — we shall then get a new set of

---

* It is shown in this article, that the assumption made in GOST 2331-43 (All-Union Standard), during analysis of steels for C, S, and P, can be represented by an equation: GOST assumes $\frac{2\sigma_{\text{reproducibility}}}{\sqrt{n}}$, where $\sigma_{\text{reproducibility}}$ is the square of the reproducibility error; n is the number of replicates on which analysis is based; for carbon n = 4; and for sulfur and phosphorus n = 2.

** In the overall balance of the errors of a chemical analysis, the reproducibility error plays a small part; accordingly, some authors [14] agree that mathematical statistics should not be used for exposing the actual errors of a chemical analysis.

measurements, which differs essentially from the first set — here again, a magnitude which was constant in the first instance has become a variable. At the same time, the statistical ensemble, consisting of a number of measurements of one test object in different laboratories, may differ essentially from the statistical ensemble, obtained from a number of analyses of another test material in the same laboratories. The variation coefficient (relative square error) obtained for one of these ensembles, does not permit one to forecast what the analogous value for another ensemble will be; the laws of distribution of these ensembles can also vary. This is illustrated by the histograms borrowed from the literature [10], for the results of the analysis of two silicate samples of granite and diabase for their CaO and MgO content, which was carried out in 24 laboratories in various countries.

4. Finally, let us consider the statistical ensemble, consisting of a number of measurements of standards differing in composition (of one type) carried out in one laboratory in the course of a short time interval. We shall take the certified results (i.e. the ones given with the samples) as being the center of scatter — we shall calculate the error for each sample as a difference between the certified results and the mean values of the analytical results, and we shall express the errors in terms of relative percentages. This rather unusual statistical ensemble we shall consider in greater detail — it is of particular interest, since, if in the course of practical work, for the control of the correctness of an analysis, one should take only one SS as well as the unknown samples to be analyzed, then these samples together with the standard sample can be regarded as a selection from the statistical ensemble defined above.

In the study of the relative errors of test samples which differ in composition, some of the active factors which act in a constant fashion become variables, since the magnitude of the relative errors, introduced by the constant factors, depends, in a number of cases on the concentration of the test component. E. g. during gravimetric analysis, impurities in the precipitate as the result of insufficient purity of water, or reagents, contamination by the containing vessel, etc. can give a relative error which depends on the concentration of the test component. Coprecipitation of elements which accompany the test element gives a relative error which depends on the concentration of both the test component, and on that of the accompanying elements. Titers and factors can also depend on the concentrations of accompanying elements in volumetric and photocolorimetric methods of analysis. Characteristics of the phase composition of test samples (on which the solubility of test samples depends) can, in certain instances, give a random error for the number of measurements of various test samples considered by us.

The following is of interest as an example: the frequently recurring instance of an error which depends on the concentration of test component. If there are several standards, then, in the case of volumetric and photocolorimetric analysis, it is possible to construct graphs in which concentration is plotted along the abscissa, and the number of cm³ used for titration on the ordinate; then the cotangent of the angle slope of this line will be the titer, while the segment cut off along the ordinate will be the number of cm³ used for titrating — the "blank" (Fig. 2). Determination of the titer by means of several SS does not lead to doubt. Nevertheless, the analyst has usually only one SS at his disposal, and the number of cm³ used for the "blank" is used as the second point. Direct determination of the "blank" is bound up with a number of difficulties as a result of the weak color — the relative error in determining this point is very large. In addition, it must be borne in mind, that in the "blank", only the concentration of test component should be equal to zero, while the concentrations of the other components (base and accompanying elements) should remain unchanged — it is impossible to fulfil this requirement in practice during direct experimental determination of the "blank". Determination of the titer by means of an unreliably determined "blank", is equivalent to exchanging the true curve, designated in Fig. 2, by a complete line, by an incorrect curve designated by the dotted line. Comparison of these two lines show that, in this case,

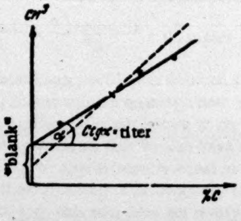


Fig. 2. Graphical determination of the titer by means of several standard samples (complete line) and by means of a standard sample (dotted line).

the magnitude of the error and its sign, depend on the position of the test sample relative to the standard, by means of which the titer is established. In instructions, it is usually stated that a SS should only be used for establishing the titer, in the analysis of samples approximating in composition to the given SS; this leads to a decrease in the error, but, in principle, does not eliminate it*. We analyzed 40 samples of slag for their FeO_{total}, and calculations were made by two methods – by means of a graph constructed on the basis of several standards (combined SS's), and by means of a titer which was determined on the basis of one SS and a blank, – the deviation which was determined solely by this fact, gave a relative square error of 3.7%.

Thus, in a statistical ensemble, consisting of the analysis of a number of samples differing in composition, a new random error appears, which is transformed into a constant, if one is confined to a number consisting of the analysis of one test sample. Determination of this value is bound up with considerable difficulties. If we have a series of standards and carry out calculation of the errors with respect to the certified results, then we get the total error:

$$\sigma_{\Sigma} = \sqrt{\frac{\sigma^2_{\text{reprod.}}}{n} + \sigma^2_{\text{random chem.}} + a^2}, \qquad (1)$$

here $\sigma_{\text{reproducibility}}$ is the reproducibility error for one analysis, n is the number of replicate tests, on the basis of which the analysis is carried out; $\sigma_{\text{random chem.}}$ is the random error, determined by the characteristics of the chemical and phase composition of the test samples; a is a constant error** (displacement of the actual scatter center of the random errors with respect to the specified results, on the basis of which the errors are calculated).

If we have a series of test samples which differ in composition, and which have been analyzed by methods which differ in principle in one, or several laboratories, then the deviation in the analytical results will be represented by the following error:

$$\sigma_{\Sigma\ \text{I-II}} = \sqrt{\frac{\sigma^2_{\text{reprod. I}}}{n_{\text{I}}} + \frac{\sigma^2_{\text{reprod. II}}}{n_{\text{II}}} + \sigma^2_{\text{random chem. I}} + \sigma^2_{\text{random chem. II}} + (a_{\text{I}} - a_{\text{II}})^2}, \qquad (2)$$

here the indices I and II denote the errors of two different methods; the values a_{I} and a_{II} are calculated algebraically. Finally, if a series of samples are analyzed in two different laboratories by the same method, or by methods which only differ in details, then the analytical results of the two laboratories can, generally speaking, be correlated between each other, when

$$\sigma_{\Sigma\ \text{I-II}} = \sqrt{\frac{\sigma^2_{\text{reprod. I}}}{n_{\text{I}}} + \frac{\sigma^2_{\text{reprod. II}}}{n_{\text{II}}} + \sigma^2_{\text{random chem. I}} + \sigma^2_{\text{random chem. II}} - 2r\sigma_{\text{random chem. I}}\sigma_{\text{random chem. II}} + (a_{\text{I}} - a_{\text{II}})^2}, \qquad (3)$$

here r is the correlation coefficient between the analytical results of the two laboratories. In this case, $\sigma_{\varepsilon\text{I-II}}$ is a very indeterminate quantity; here we have an equation with many unknowns, and, at the same time, the correlation coefficient is not known to us. In a special, limiting case, the work of the two laboratories may be in such good agreement, that we can have $r = \sim 1.0$; $\sigma_{\text{random chem. I}}$ is approximately equal to $\sigma_{\text{random chem. II}}$; a_{I} approximately equal to a_{II}. In this case, $\sigma_{\varepsilon\text{I-II}}$ will be determined only by the reproducibility errors. Thus, if during interlaboratory control, when the same type of method is used, a small value is obtained for $\sigma_{\varepsilon\text{I-II}}$, this still does not testify to the real absence of errors. During particularly careful chemical analysis, e.g. the preparation of standards, very often, intensive and expensive efforts are directed at achieving good agreement for the results of chemical analysis in different laboratories, when it is quite possible, that in a number of cases, these efforts are really only directed at getting the correlation coefficient to approach unity, and not to an actual attempt at cutting down the errors.

---

* The use of SS for establishing the titer, from a formal point of view, can be regarded as an unjustified introduction of the same correction to test samples differing in their composition.

** The use of dispersion analysis can be recommended for individual calculation of errors entering (1), and for the determination of their significance. We intend to devote a separate article to this question.

It is exceedingly important that we clear up the law of the distribution of this new random magnitude. We shall consider this question primarily on theoretical grounds. According to the central limiting theorem of Lyapunov, total θ of independent random magnitudes $x_1, x_2, \ldots x_\nu$ for a sufficiently large ν, has a normal distribution, even when the independent random magnitudes $x_1, x_2 \ldots$ have an arbitrary distribution under the condition that all random magnitudes considered are of approximately the same order, i.e. there should not be such random values among the magnitudes $x_1, x_2, \ldots x_\nu$, as are greater than most of the other magnitudes. In the special case, where the unknown variables are distributed normally, the sum will be distributed normally for any ν. In the case we are considering viz.,a number of measurements of samples differing with respect to their composition, we have to deal with a large number of independent variables (their number, is, of course, greater than we enumerated above); the laws of distribution of these variables, are, generally speaking not known to us, but, we can at least assume that when methods which have been worked out well are used, and the laboratories in which the work is carried out are properly organized, the dominating factors should be absent — this permits one to assume that the random error, whose scattering is characterized by $\sigma_{\text{random chem.}}$, should obey Gauss' law. The normal law immediately breaks down, if one of the components, even the test component, varies within very wide limits, and is converted in this way into a dominating factor. E. g., there is hardly any sense in uniting in one statistical ensemble, test samples in which the test component varies within limits ranging from some hundredths of a percent to 1-10%; but, if for some reason, such unification is carried out, we get a correlation link between the value of σ and the concentration of the test component, as shown in Shaevich's work [5]. Thus, the random error which is characterized by the characteristics of the chemical composition of the test samples, will have a normal distribution only when certain conditions are fulfilled; for reproducibility errors, these conditions are almost always fulfilled automatically, and consequently, for reproducibility errors, there is practically always a normal distribution.

When considering the distribution of analytical results for samples differing in composition, it is always necessary to take into account the presence of a constant factor, which shifts all the deviations to one side, as a result of which one gets an asymmetric distribution of signs. Only the absolute magnitude of the errors and their distribution are of essential significance in analytical work. If we confine ourselves to the consideration of absolute magnitudes only*, then we get the following distribution function:

$$\varphi(x) = \frac{1}{\sqrt{2\pi}\cdot\sigma_0}\left[e^{-\frac{(x-a)^2}{2\sigma_0^2}} + e^{-\frac{(x+a)^2}{2\sigma_0^2}}\right], \tag{4}$$

here σ_0 is the mean square deviation of the original normal distribution; a is the shift in the center of this distribution. In the case where $a/\sigma_0 < 1.0$, distribution (4) can be replaced by the function:

$$\varphi(x) = \frac{2}{\sqrt{2\pi}\cdot\sigma_0} e^{-\frac{x^2}{2\sigma_0^2}} \tag{5}$$

this is a Gauss distribution on the basis of the descending side with doubled ordinates. Function (5) can, to a first approximation, describe the statistical ansemble which we are considering, which consists of a number of samples differing in composition, they are formed in such a way that a dominating factor is absent. Let us consider as an example the analysis of 50 slag samples for CaO, SiO_2, and total Fe, which was carried out in two different laboratories by two different methods. In Table 1 are given the results characterizing the distribution of errors for interlaboratory control of slags; here we have a clear-cut case of sign assymmetry. On changing over to absolute values of the errors, we get a distribution, which, as calculation of the criterion of agreement shows, is described fairly well by distribution function (5).

---

* One often comes up against consideration of the absolute values of the deviation in machine construction, during a study of the quality and accuracy of production — this question is treated in detail by Borodachev [11].

TABLE 1

Components determined	σ_s I–II, in %	Number of errors with the same sign in %	Probability of a random deviation from distribution (5) according to Pearson	according to Kolmogorov
CaO	6.05	93	0.13	0.79
SiO_2	8.5	98	0.08	0.33
Total Fe	5.7	24	0.41	0.39

Taking into account the normal distribution of errors determined by the characteristics of the chemical and phase composition of test samples, one can make a critical approach to the question of how it is possible to establish reliability limits for chemical analysis, if standard samples are used for this purpose. We shall start off with a schematic and rather abstract consideration of this problem: let us assume that we analyze n standards at the same time as the unknown test samples; at the same time, we assume that standards and test samples belong to one general set, the scatter of which is determined by $\sigma_{\text{random chem. general}}$. One can solve the problem of the upper possible limit for the value of $\sigma_{\text{random chem. general}}$, if $\bar{\sigma}_{\text{random chem.}}$ is known on the basis of analysis of standards and a comparison of these results with certified results ($\sigma_{\text{reproducibility}}$ is not taken into account, since it is assumed that each standard has been made from a large number of replicates). In this case:

$$\sigma_{\text{random chem. general}} = \frac{\sqrt{n-1}}{\sqrt{\chi^2}}\,\bar{\sigma}_{\text{random chem.}} \qquad (6)$$

the value of χ^2 is given by Pearson's distribution $P(\chi^2, n-1)$.

Further, if the center of displacement a (the mean relative deviation from certified results) is determined by means n-standards (standard samples), then it would be incorrect, during the analysis of some unknown test samples to expect a deviation from the true content within the limits of the magnitude of a. The maximum possible deviation of the relative error of analytical results from the center of the displacement a is determined by the equation:

$$(a - x_{an}) = t \cdot \sqrt{\frac{n+1}{n}}\;\bar{\sigma}_{\text{random chem.}} \qquad (7)$$

where t is given by Student's distribution $S(t, n-1)$. Equations (6) and (7) can be solved for any $n \geq 2$; having set a reliability of 0.95, we get the following solutions

$n = 2$; $\sigma_{\text{random chem. general}} = 16\bar{\sigma}_{\text{random chem.}}$; $(a - x_{an}) = 16\bar{\sigma}_{\text{random chem.}}$

$n = 3$; $\sigma_{\text{random chem. general}} = 4.4\bar{\sigma}_{\text{random chem.}}$; $(a - x_{an}) = 5.0\bar{\sigma}_{\text{random chem.}}$

$n = 4$; $\sigma_{\text{random chem. general}} = 2.9\bar{\sigma}_{\text{random chem.}}$; $(a - x_{an}) = 3.6\bar{\sigma}_{\text{random chem.}}$

. . . .

$n = 10$; $\sigma_{\text{random chem. general}} = 1.7\bar{\sigma}_{\text{random chem.}}$; $(a - x_{an}) = 2.4\bar{\sigma}_{\text{random chem.}}$

These calculations show that, even in this case, when standards and test samples can be regarded as a random choice from a set with normal distribution, for establishing reliability limits for a small number of standards, it is necessary to multiply $\bar{\sigma}$ random chem. by a very large coefficient. From this it becomes quite obvious why, sometimes, the analysis of some sample or other gives a result which is far from the true content of the test component, though the standards which were analyzed at the same time as the test sample gave sufficiently good agreement with the certified results. In particular, these calculations permit one to understand why such large errors can be obtained during inter-laboratory control of slag (Table 1), though both laboratories check the correctness of their work on one and the same standards.

In practical work, application of formulas (6) and (7) for establishing confidence limits is connected with certain difficulties*, since in such cases the following conditions must be fulfilled: standards and test samples must be a random choice from a set, in which there is no very marked deviation from a normal distribution. The latter condition is deliberately formulated rather loosely, since, it is known from published results [12], that experimental verification has demonstrated the possibility of using Student's distribution, on which formula (7) is based, even when deviation from a normal distribution is observed in the general set. If test samples and standards (with respect to the test component) lie within the concentration range, the limits of which do not differ by more than a factor of 2, then there is no foundation for fearing a large deviation from normal distribution. Test sample and standards can be regarded as random choices from one and the same set, consisting of samples differing with respect to composition, if the standards differ essentially from one another in their chemical composition. In order to verify the possibility of using equation (7) under the restrictions indicated, we prepared in our laboratory 10 synthetic slag standards which differed in their chemical composition; each of these standards was then subjected to replicate analysis using the same simplified methods as were used for a series of tests. The standards were divided into groups in which the test component content was changed within the limits 1:2 for each group; by means of equation (7) the ratio of the maximum expected error to the actually determined maximum deviation from the certified results was calculated. Results of these calculations are given in Table 2. Here, in the first short line are given results obtained for calculations for n = 3; at the same time three standards were deliberately chosen such that they had a minimum deviation from the certified results.

TABLE 2

	CaO	SiO_2 wt.		SiO_2 Φ/K		$Fe_{tot.}$	Mg	MnO		Al_2O_3	
Concentration range	22–47%	12–25%	25–38%	12–25%	25–38%	3–7%	3–6%	2–4%	8–10%	1–2%	3–7%
Ratio found error to calc. error [by eq. (7): n = 3, α = 0.95].	0;7	2:1	3;9	1;5	1;3	2:0	1;3	1;7	1;2	3:1	0:8
Ditto for $n = 4–9$	0:8 $n = 9$	1:4 $n = 5$	—	2:0 $n = 5$	—	— $n = 6$	1:7 $n = 4$	2;1	1:0 $n = 4$	—	0:8 $n = 5$

---

* Formula (7) is usually used for solving the problem of whether the (n + 1) determination is compatible with the other n measurements. Here, it is necessary to solve the opposite problem: to lay down conditions under which analysis of n standards will be compatible with the analysis of the (n + 1) test sample, and then, on the basis of equation (7) establish confidence limits for analysis of test sample.

The results in Table 2 show that, under certain conditions, equation (7), for $n \geq 3$, can be used for establishing reliability limits. Formally, equation (7) can also be used for $n = 2$ •; nevertheless, establishment of reliability limits for $n = 2$, is hardly worthwhile in practice, since, in such cases, on account of the small number of standards, one would have to use a very large coefficient, and this, in many cases, will inevitably lead to very high values for the reliability limits.

Reviewing the position, one can indicate the following methods of evaluating errors, determined by the characteristics of the chemical and phase composition of test samples.

1. The Use of Standards. Reliability limits can be established by means of formulas (6) and (7), when the following conditions are fulfilled: a) number of standards $n \geq 3$; b) test samples and standards are chosen so that the test component lies within a concentration range, the extreme points of which are in the ratio of 1:2; c) the standards should differ essentially from each other with respect to their chemical composition (in some cases their phase composition as well). Despite all limitations, this method is not free from a number of arbitrary assumptions and its application in each specific case requires a careful analysis of all available material.

2. Checking the Same Sample by Methods which Differ in Principle. In such cases one comes up against the following difficulties: a) even in the case of methods which differ in principle, analytical results may be related to each other in a correlative way; this no doubt happens, if, during development of one method, one takes as a basis the results of another, i.e. to consciously produce agreement between the two methods••. This is confirmed by the fact that sometimes the results of analysis of samples carried out within one laboratory by methods which differ in principle, differ less among themselves than the analyses of the same samples carried out in different laboratories but by the same method; b) if, even by some indirect methods it has been established that correlation is absent in the results of an analysis carried out by two different methods, equation (2) cannot be solved, since there are several unknowns; it must be replaced by the equations:

$$\sigma_{\Sigma\,I-II} = \sqrt{\sigma^2_{\Sigma I} + \sigma^2_{\Sigma II}}; \quad \sigma_{\Sigma I} = \sigma_{\Sigma II}; \tag{8}$$

it is only by means of this method, which is essentially a completely arbitrary method, that it would be possible to have a rough evaluation of the error we are interested in for each method taken separately.

3. Analysis of test samples, carried out in different laboratories by the same method, or by methods which differ very little from each other, can give a correct representation of the actual mistakes only in the case where the results of the laboratory do not agree among themselves, i.e. if the correlation coefficient in equation (3) is near to zero. In such a case, again, equation (3) must be quite arbitrarily substituted for by equation (8).

4. Finally, it is possible to study the reasons for the existence of errors determined by the characteristics of the chemical composition of test samples•••. From a formal point of view this is equivalent to a change-over from random errors to systematic ones. If the errors of a chemical analysis were confined to reproducibility errors and systematic errors, the reason for the appearance of which is known and can be firmly established, the question of calculation of errors would be solved very readily.

• For $n = 1$, the mathematical scheme considered is not applicable. In this case, the deviation between certified results and the mean analytical result for the standard cannot be resolved into a variable and a constant component.

•• E.g. in order to get agreement between the results of spectrographic and chemical analysis, special precautions are often resorted to: choosing special excitation conditions, parallel displacements of graphs for samples differing in composition, breaking the graphs, etc. It is possible that in certain cases, perhaps rare, it may also be necessary merely to increase the value of the correlation coefficient in equation (3) to values approximating unity.

••• E. G. compilation of a complete material balance for gravimetric methods of analysis using spectrographic methods of study, of the method of tagged atoms, and other methods for studying composition of precipitates, filtrates, etc. (an example of such a study is given in [13], where the use of spectrographic methods for correcting gravimetric analysis is demonstrated).

Analysis of chemical errors, carried out in this paper, shows that all possible methods of evaluating the correctness of a chemical analysis, apart from the last one, are based on a number of arbitrary assumptions; accordingly, they must be considered as only rather rough orientating methods. As far as the last method is concerned – studying the reasons for the mistakes, – it is free from any arbitrary assumptions, but is characterized by being extremely cumbersome and accordingly can only be seldom used in practice.

SUMMARY

Chemical analysis is a complex measuring process, which differs in principle from elementary measuring processes which are dealt with in metrology. In chemical analysis, in addition to the random error of reproducibility, there is one further random error, which is determined by the characteristics of the chemical (and sometimes, phase) composition of test samples. The distribution law of this error is considered. Various methods of evaluating the magnitude of this error are critically considered; conditions under which standards can be used for establishing reliability limits are established.

Received May 18, 1955

LITERATURE CITED

[1] E. E. Gracheva, J. Anal. Chem. 7, 1, 48 (1952) (T. p. 51)*.

[2] N. P. Komar, J. Anal. Chem. 7, 6, 325 (1952) (T. p. 361)*.

[3] S. A. Gusinskaya, J. Anal. Chem. 9, 4, 245 (1954) (T. p. 273)*.

[4] N. I. Kambulatov, S. A. Genshaft, and B. V. Nalimov, Factory Lab. 19, 1, 1, 115 (1953).

[5] A. B. Shaevich, J. Anal. Chem. 9, 6, 373 (1954) (T. p. 415)*.

[6] B. V. Glivenko, "A Course in the Theory of Probability", State United Sci. Tech. Press, 1939.

[7] N. Harley and K. Bukh, "Introduction to the Theory of Probability and Mathematical Statistics", Foreign Lit. Press, 1951.

[8] A. M. Dlin, "Mathematical Statistics in Technics" Soviet Science, 1951.

[9] N. A. Borodachev and B. M. Shchigol, "Machine Construction. Encyclopaedic Reference Book" Vol. 1, 1947.

[10] H. F. Fairbairn, Geological Survey Bulletin, 980 (1951).

[11] N. A. Borodachev, "Analysis of the Quality and Accuracy of Production" State Sci. and Tech. Press on Literature on Machine Building, 1946.

[12] V. I. Romanovsky, "Mathematical Statistics" State Planning Commission Press, 1939.

[13] P. R. Wilkinson, J. A. Gibson and A. J. Headlee, Anal. Chem. 26, 4, 764.

[14] A. K. Babko, Factory Lab. 21, 3, 269 (1955).

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

A MANOSTAT AND RECEIVER FOR VACUUM DISTILLATION IN COLUMNS

M. I. Rosengart, A. L. Liberman, and D. M. Dubinin

Institute of Organic Chemistry, USSR Acad. Sci., Moscow

Analytical distillation on columns is widely used during analysis of mixtures of organic materials in order to get accurate fractionation. In recent years such distillations have more and more often been carried out not only at atmospheric, but also at reduced pressures. For working under vacuum it is easy to use normal laboratory columns with packing of various types, e.g. of the type we described previously [1]. Nevertheless, in order to carry out successful analytical distillations, the columns should be provided with certain additional attachments: first of all with a manostat – an apparatus which ensures a constant pressure in the system during distillation –, and a receiver, by means of which it is possible, without interrupting distillation, to select an unlimited number of fractions.

Carrying out analytical distillations under a vacuum, without the aid of a manostat, requires practically undivided attention from the analyst if a constant pressure is to be maintained in the system; even then the results obtained are not so reliable as those that can be obtained when the pressure is automatically regulated. Actually, during vacuum distillation, comparatively small variations in the pressure have a relatively large effect on the temperature of the saturated vapor in equilibrium with liquid, and is considerably greater than at atmospheric pressure. As an example one can cite results for variation of the saturated vapor in equilibrium with the liquid, with the pressure, for the case of diethylphthalate, 1-ethylnaphthalene, and 1,7-dichloroctamethyltetrasiloxane [2]. According to calculation, a change in pressure of 1 mm leads to a change in temperature of the vapor of 6° in a vacuum (at 3-4 mm) and to less than 0.1° at atmospheric pressure. Thus, a change in pressure during vacuum distillation leads to a change in the temperature of the saturated vapor, without changing its composition; it destroys the equilibrium established, and, consequently, affects trickling, reflux number, and other operational conditions in the column. Moreover, in various parts of the system the pressure does not change evenly, and as a result it may show up differently on the thermometer bulb and on the manometer; this leads to incorrect determination of the boiling temperature.

A number of manostats are described in the literature which can be used for use with laboratory columns [3]. In the present communication we described a manostat which is distinguished by its simplicity of construction; it is convenient to use, and gives good results in practice.

When analysis is carried out with the aid of rectification, usually a distillation curve is "taken", i. e., a curve is drawn on the basis of the volume of distillate registered and the vapor temperature; this permits one to get an idea of the qualitative and quantitative composition of the mixture distilled. When carrying out analytical distillation under vacuum, it is necessary to provide the column with a receiver which will enable many fractions to be selected without interrupting the readings necessary for constructing a distillation curve. A receiver of this type is described in the present article; this has already been used with success in our laboratory and is now being manufactured by one of our factories.

Manostat. The manostat is an all-glass one (Fig. 1). Mercury is used as the sealing liquid; it is poured into chambers A and B till on opening tap 3 it touches all the surface of the lower edge of the porous glass disc 1.

The principle of the operation of the manostat consists of the following: the requisite pressure is established in the system, after which the taps are closed (Fig. 1); a "standard" pressure will then be maintained in chamber A. If the pressure in the system, and consequently in chamber B, connected with the system isolated from the pump by

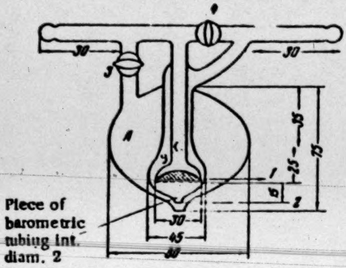


Fig. 1. Manostat.

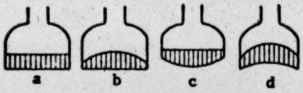


Fig. 2. Test forms of the porous discs.

means of tap 4, exceeds the pressure in A, then the mercury will flow back from A into B, since they are connected to each other, like communicating vessels, through opening 2. As a result, the level of mercury in B drops a little and opens up the porous disc a little. Then, through the latter, air will be sucked from B, into C which is connected with the pump until a pressure equal to the standard pressure in A will be established in B, and consequently through all the system. When this occurs, the level of the mercury in A and B will become equal and the mercury again closes the porous disc, cutting off, thereby, the exit of the air from the system into C.

During actual operation, all of this is realized as follows. The manostat is fitted into the system between manometer and vacuum pump. The system is evacuated on opening the manostat taps. When the manometer indicates the requisite pressure, both manostat taps are immediately closed. Under these conditions, for normal operation of the manostat, it is necessary to have a pressure drop of not less than a certain definite pressure value (see below) between the vacuum pump and the system in which constant pressure is being maintained.

If the amount of mercury in the manostat corresponds exactly to the level indicated above, the manostat will, in the course of many hours, maintain a constant pressure in the system without further attention from the operator. If the amount of mercury is greater or less than the amount indicated, then the pressure finally established in the system will differ from the pressure at which the taps are closed to a greater or lesser extent.

When the operation is finished, it is first of all essential to open both manostat taps immediately; air can then be let in. In fixing the manostat, it is necessary to make sure that its porous disc is arranged as horizontal as possible, even visually, and also that the manostat is protected from appreciable temperature changes in the surrounding medium.

As tests we carried out showed, operation of the manostat depends on the shape of the porous disc and on its porosity. Results of tests on discs of different porosity showed that a porous disc from a No. 1 filter is not suitable for a manostat, since the mercury filters through it even for a pressure difference on opposite sides of only 30 mm Hg. Mercury only starts to filter through a No. 2 filter at a pressure difference greater than 150 mm. Discs made from No. 3 and 4 filters permit work at any residual pressure right up to 760 mm; nevertheless, the rate of suction of air through a filter No. 3, and even more so through a No. 4 is considerably less than through a No. 2 filter. As a result of this, a manostat fitted with a disc made from a No. 2 filter best maintains a constant pressure in the event of an accidental or necessary letting of air into the system. Moreover, the minimum necessary pressure drop between pump and the system amounts to only 4-5 mm when a No. 2 disc is used, while it is not appreciably greater in the case of a No. 3 or a No. 4.

Thus, for regulating the pressure below 150 mm (and this is more often the case than not) a porous plate made from a No. 2 filter is best suited. When this is done, it cannot be assumed that the pressure difference between B and C exceeds 150 mm, i.e. one should not close the manostat taps until the pressure in the system has dropped below 150 mm, in order to avoid filtration of the mercury into C. If it is necessary to distill at pressures higher than 150 mm, one should use a manostat fitted with a porous disc made from a No. 3 filter. If however, only a manostat fitted with a No. 2 disc is available, one can still use such a manostat, as long as one ensures that air is let into a line connecting manostat with pump. This bleeding, which can be achieved by means of a T-piece fitted with a tap or clamp, is used for lowering (down to 150 mm or even less) the pressure difference between B and C.

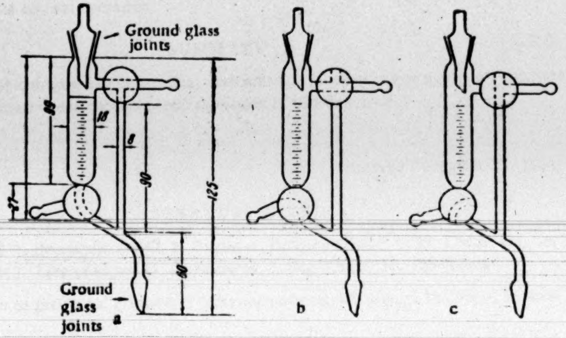


Fig. 3. Receivers: a) In the operating position; b) position of taps while switching cylinders; c) position of taps while evacuating the cylinder.

The shape of the disc, as was shown above, also affects the work of the manostat. Of the four types of porous glass discs tested, best results were given by the plano-convex disc (Fig. 2b). The use of such a disc cuts down the time required to establish a constant pressure, and increases the sensitivity of the manostat to changes in pressure in the system when air is let in. Discs of the shape indicated can be prepared when constructing a manostat by machining a lump of porous glass filter 5-7 mm thick. On fusing the disc in the apparatus, it should be tested for the minimum pressure at which filtration of mercury through the pores starts.

Receiver. The receiver is also an all-glass one. (Fig. 3). The bottom tap of the receiver is crescent shaped while the upper tap is a three way one. The ground glass joint to which the calibrated cylinder is connected, should be a normal one, or several cylinders can be fitted to one joint. The cylinders should be calibrated in 0.2 or 0.1 ml. Such calibrations of 0.2 or 0.1 ml should also be provided on the upper part of the receiver to 2/3 of its height.

For establishing the requisite vacuum in the column and for taking distillate samples, the position of the taps should be that shown in Fig. 3a. For switching cylinders, the taps should be rotated into the position shown in Fig. 3b. In doing this, it is necessary first of all to turn the upper tap, and only after this has been done is the lower one turned. As a result, the pressure in the cylinder will become equal to atmospheric, after which the cylinder can easily be removed and replaced by another. The lower tap is then turned to the position shown in Fig. 3c, after which the upper tap is also carefully turned into the respective position, taking care, by observing the manometer, that the pressure does not change too rapidly. When the pressure in cylinder and system have returned to their former value, the upper tap is turned into the position corresponding to that shown in Fig. 3a, and the bottom tap then turned to its corresponding position. Since the air in the lower tap is still at atmospheric pressure, the tap must be turned very carefully.

Since the top part of the receiver is calibrated, taking of distillates need not be stopped during change-over of cylinders; accordingly, this operation does not interfere with getting the requisite results for constructing a distillation curve within the coordinates, distillate volume – temperature, which is usually necessary for evaluating the quantitative composition of the mixture being distilled.

If the manostates are imperfectly made (poor fit of tap 4, poor finishing of the lower side of the filter disc, etc), the pressure in the system will continue to drop very slowly even after closing both taps. In such cases, it is recommended that a T-piece be fitted between manostat and manometer; to one end of this T-piece is connected a piece of barometer tubing (internal diameter ~ 0.5 mm) with one end drawn out into a capillary. The capillary should be narrow enough to ensure bleeding in of air into the system without producing a visible change in pressure. Such bleeding in of air will usually compensate completely for defects in the preparation of the manostat, and will ensure normal operation.

SUMMARY

Descriptions are given of a simple and convenient manostat and receiver respectively, for analytical distillations on rectifying columns under vacuum; their operation is also described.

Received December 22, 1954

LITERATURE CITED

[1] B. A. Kazansky, M. I. Rozengart and O. P. Solovova, Bull. Acad. Sci. USSR, Chem. Sci. Section, 97 (1941); B. A. Kazansky, A. L. Liberman and O. D. Sterligov, J. Org. Chem. 13, 125 (1943).

[2] D. R. Stell, "Tables of the Vapor Pressure of Individual Materials", Foreign Lit. Press, Moscow, 1949.

[3] F. Todd, Ind. Eng. Chem., Anal. Ed., 20, 1249 (1948).

BRIEF COMMUNICATIONS

THE USE OF CHROMATOGRAPHY IN QUALITATIVE ANALYSIS

Stoiko Yankov

Bulgaria

Detection of Mn^{2+} in the Presence of Cr^{3+}. During detection of small amounts of Mn^{2+} with hypobromite in the presence of Cu^{2+} as a catalyst, the color from the manganese is masked by the yellow color of the CrO_4^{2-} ions formed.

Tests which we carried out showed that satisfactory results can be obtained by the following method: 0.05 ml of test solution, acidified to 0.6% HCl, is passed through a micro-column packed with Al_2O_3 containing a 10% mixture of KBr and $KBrO_3$ (1 : 1). After some time (4-5 minutes) a brown strip of MnO_2 appears in the middle of the wide yellow band. If the 0.05 ml of solution contains 0.0035 mg of Mn, then after 10 minutes, only a weak brown color of MnO_2 is formed. On heating the column with an electric lamp (60 watt), the brown color of MnO_2 appears at even lower amounts of manganese (0.0017 mg Mn in 0.05 ml).

Micro-Analytical Detection of Co^{2+} in Admixture with Fe^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, Zn^{2+}, Al^{3+}. Through a micro-column packed with Al_2O_3 is passed successively 0.05 ml of test solution, 2-3 drops of a saturated solution of NH_4SCN and 2-3 drops of acetone. After several minutes a blue ring appears if Co^{2+} is present. The limit of identification is 0.4 γ Co. The reaction sensitivity depends on NH_4SCN concentration; with decreasing NH_4SCN concentration, the sensitivity drops off.

Co^{2+} can be detected in a neutral solution in 5-7 minutes; in acid solution it takes 10-12 minutes.

Co^{2+} should be detected in neutral solution, when the red color of Fe^{3+} hardly appears and the blue band is clearly defined.

In acid solution a rather intense red color develops which may interfere with Co^{2+} detection; accordingly, when working with acid solutions, it is necessary to use a mixture of Al_2O_3 plus NaF in a ratio of from 1 : 8 to 1 : 10. In such cases, the red color does not appear even at HCl concentrations up to 2%. The reaction sensitivity however drops to 1.5 γ.

Received June 17, 1955

BLANK
PAGE

THE DICHROMATE METHOD OF DETERMINING PIPERAZINE

A. A. Chemerisskaya

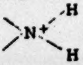
S. Ordzhonikidze All-Union Chemico-Pharmaceutical Institute of Scientific Research, Moscow

In Castiglioni and Nivoli's paper [1], a method is described for the quantitative determination of piperazine as its slightly soluble bichromate salt. According to tests we have carried out, this method is capable of giving good results which are in agreement with results of the picrate method [2], as long as the following modifications are introduced:

1. Castiglioni and Nivoli state that piperazine dichromate has the following composition: $C_4H_8N_2 \cdot Cr_2O_7$. The formula $C_4H_{10}N_2 \cdot H_2Cr_2O_7$ is however more probable for piperazine dichromate – by analogy with other compounds of this type. This formula has been confirmed by the results of elemental analysis and by spectroscopic studies.

In order to decide on the correctness of one formula or the other for piperazine dichromate, the hydrogen content of the latter is of decisive importance. Castiglioni and Nivoli's formula indicates that piperazine dichromate contains 8 hydrogen atoms, while the formula $C_4H_{10}N_2 \cdot H_2Cr_2O_7$ contains 12 hydrogen atoms. At the same time, the content of the other elements depends only to a very small extent on the two formulas for the composition of piperazine dichromate; since, in this case the molecular weights according to the two formulas are 300.14 and 304.172, in which the difference is small. The results given in Castiglioni and Nivoli's article for the determination of nitrogen and chromic oxide can hardly be accepted as sufficient for a final decision as to which formula is correct, since the difference in the nitrogen content amounts to only 0.11%, while that in the Cr_2O_3 contents amounts to 0.67%. The following results were obtained during the determination of the hydrogen and carbon contents:

Found %: H 3.89; 3.93; 3.96; C 15.61; 15.80; 15.75.
Calculated for $C_4H_8N_2 \cdot Cr_2O_7$ %: H 2.69; C 16.01.
Calculated for $C_4H_{10}N_2 \cdot H_2Cr_2O_7$ %: H 3.98; C 15.79.

Comparison of the infra-red spectra of piperazine and piperazine dichromate carried out by coworker Yu. N. Sheinker of our Institute, showed that in the spectrum of piperazine at 1600 cm^{-1}, absorption bands appear which are characteristic of the NH_2^+ group, and are determined by the deformation vibrations of hydrogen atoms in it. The formation of the group  is normal for the formation of the salts of organic bases, and, accordingly, is in good agreement with the formula suggested by us. At the same time, when such a group is present, it is difficult to visualize the piperazine derivative as having a formula of $C_4H_8N_2 \cdot Cr_2O_7$.

2. The conversion factor used by Castiglioni and Nivoli for converting the dichromate to piperazine is 0.2802. The numerical value given for this factor is quite incomprehensible even when one used their assumed formula of $C_4H_8N_2 \cdot Cr_2O_7$. In our opinion, the conversion factor to anhydrous piperazine should be 0.2832, and to the hexahydrate of piperazine – 0.6386.

3. When working with 10% solutions of piperazine hexahydrate, the length for which the solutions are kept after addition of chromic acid can be cut down from 6-7 hours to 15 minutes. For this purpose, it is necessary to use 2 ml of solution (40 g CrO_3 in 100 ml water) and to cool the reaction mass in ice.

On applying the method indicated to the analysis of samples, the values found by the dichromate method for piperazine hexahydrate were 98.36 and 98.35%, while by the picrate method, the values found were 97.80 and 98.05%.

SUMMARY

Castiglioni and Nivoli's method for the determination of piperazine has been made more accurate.

Received February 15, 1955

LITERATURE CITED

[1] A. Castiglioni and M. Nivoli, Z. Anal. Chem., 138, 186 (1953).

[2] Ch. Morin, Ann. pharm. franc. 6, 512 (1948); C. A. 43, 7869.

A FRACTIONAL REACTION FOR COBALT*

M. A. Popov

Central Laboratory of the West-Siberian Geological Department, Novosibirsk

In describing a fractional method for cobalt, the author of article [1], made several incorrect assumptions. According to him, the following cations do not interfere with the detection of cobalt:

$$NH_4^+,\ Li^+,\ K^+,\ Na^+,\ Rb^+,\ Cs^+,\ Mg^{2+},\ Ca^{2+},\ Ba^{2+},\ Sr^{2+},$$
$$Fe^{2+},\ Fe^{3+},\ Zn^{2+},\ Al^{3+},\ Ni^{2+},\qquad Cr^{3+},\ Mn^{2+},\ Ag^+,\ Hg^+,\ Hg^{2+},$$
$$Cu^{2+},\ Pb^{2+},\ Cd^{2+},\ Bi^{3+},\ Sn^{2+},\ Sb^{3+},\ Ce^{3+},\ Zr^{4+},\ UO_2^{2+},\ Th^{4+}.$$

It is noted there, that of the cations listed, only Bi^{3+} which forms a "bright yellow or orange" complex with thiourea, masks the color of the complex compound of cobalt; copper also combines with thiourea to give a complex with a "white color", while nickel and chromium interfere because of their own intrinsic colors.

His statement does not correspond to facts, since, it is known that many cations form complexes with thiourea [2], and in doing so, use up reagent and lower the sensitivity of cobalt detection. Elements which react with thiourea, include the following:

$$Cu^{2+},\ Mn^{2+},\ Cd^{2+},\ Ni^{2+},\ Sn^{2+},\ Zn^{2+},\ Pb^{2+},\ Ag^+,\ Hg^+,\ Hg^{2+}$$

etc. Some of them, on interacting with thiourea form colored products, e.g. the compounds of univalent mercury: Hg_2Cl_3, Hg_2SO_4, $(HgNO_3)_2 \cdot 2H_2O$; mercuric oxide HgO and ferric chloride $FeCl_3 \cdot 6H_2O$ give an intensely black color; nickel chloride gives a yellow colored complex.

The shade and intensity of the color of reaction products containing the same cation, very often depend on the anion to which the cation to be tested for is connected [3]. The author also noted a difference in the shade of the blue-light blue color, obtained on triturating the various salts of cobalt with thiourea. Cobalt acetate forms reaction products having an intense ultramarine color; ferric sulfate and ferric alum a red-brown color, while nickel sulfate gives a dark blue complex with thiourea. The idea has originated of developing a so-called "molecular" qualitative analysis differing essentially from ordinary inorganic qualitative analysis carried out in solution. Using this new method of analysis it is now possible to diagnose not only individual cations and anions but frequently individual compounds and even the extent of hydration of crystals of one material.

The author follows the tradition of listing materials which interfere in the form of cations. This listing is, in principle, incorrect when it is applied to reactions between solid substances. It was noted above that the color depends on the anion also when salts of iron and nickel are triturated with thiourea. A similar relationship was also observed with other elements; thus, among the cations listed above, the chlorides of magnesium, calcium, aluminum, cerium, and to a lesser degree of ammonium, potassium, and strontium, in contrast to the nitrates, sulfates, phosphates and other salts of these elements will themselves interact with cobalt salts to form compounds which are colored blue in varying intensity. Accordingly, some of the chlorides just listed could well be used instead of thiourea.

---

* Apropos Goldberg's article [1]

Chemical transformations between solid materials in their application to qualitative analysis has hardly been studied at all so far. There are results [3, 4, 5], which permit one to postulate that the simultaneous combination in an individual chemical material of physico-chemical properties characteristic of it, such as: solubility, hydration and dissociation, pH, "chemical nature","chemical specificity", determine its behavior during its trituration with other materials. All these properties are sharply expressed individually in a solid material: they direct the course of a chemical transformation, and sharply limit the use of so called "general" and "specific" reactions to the detection of a cation or an anion respectively to a particular salt only, or to that salt in a specific state of hydration. The interfering materials listed simply as ions cannot be regarded as correct.

SUMMARY

1. Compounds of univalent mercury, mercuric oxide, and the chlorides and sulfates of iron and nickel interfere with fractional detection of cobalt.

2. The visible color effect of the reaction depends on the anion with which the test cation is linked (the nature of the cation affects the color of the reaction product during detection of the anion).

3. Interferring materials should be referred to, not as ions, but as salts of a known chemical composition, when the method of trituration of powders is used for qualitative analytical purposes.

Received November 22, 1954

LITERATURE CITED

[1] G. S. Goldberg, J. Anal. Chem. 9, 56 (1954) (T. p. 63)*.

[2] K. B. Yatsimirsky and A. A. Astasheva, J. Anal. Chem. 7, 43 (1952) (T. p. 45)*.

[3] P. M. Isakov, J. Anal. Chem. 6, 281 (1951).

[4] P. M. Isakov, "Qualitative Analysis of Ores and Minerals by the Trituration of Powder Method", State Geol. Press, 1953, p. 5 et seq.

[5] P. M. Isakov, Chemistry in School, No. 3, 45 (1954).

---

* T. p. = Consultants Bureau Translation pagination.

A NEW INDICATOR – OXINE BLUE

I. E. Lev

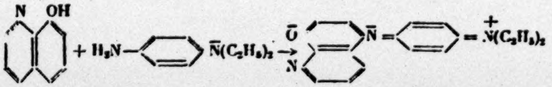
Dnepropetrovsk Metallurgical Institute

A large number of materials are known which have acid-base indicator properties; only a few of them however find practical application. This is explained by the rather strict requirements for indicators which are to be used for indicating a neutral end point [1]. Few good indicators are known for the weakly acid region. Even methyl orange and methyl red, the most widely used indicators in this range, fail to meet some of these requirements; the change in color from red to yellow during titration with alkalis lowers their value appreciably.

The synthesis and analytical properties of a new indicator – oxine blue – which can be used for neutralization purposes is described below.

Synthesis of the Indicator. 5.7 g of $HgCl_2$ and 50 ml of water are heated to the boil in a 250 ml flask. Excess NaOH is added (1.7 g in 30 ml H_2O). The freshly prepared HgO is washed a few times by decantation. To ~ 25 ml of the HgO suspension is added 1.1 g of Na_2CO_3. The solution is stirred with a stirrer until the sodium carbonate has dissolved completely. 1.84 g of p-diethylphenylenediamine sulfate dissolved in 10 ml H_2O is added, followed immediately by 1.02 g of 8-hydroxyquinoline in 50 ml C_2H_5OH. The whole is vigorously stirred for 1.5 hours while illuminated with a 300 watt lamp. 30 ml of C_2H_5OH is added and the bright blue solution filtered off from sediment; the precipitate is washed with alcohol. The filtrate is evaporated on a water bath. The resinous material is washed with 2 N NaOH, and 3-4 times with water. The product obtained is recrystallized from alcohol and dried in a desiccator over H_2SO_4; melting point 134-135°; yield 2.29 g (81.2%).

This synthesis leads to the formation of the indicator – oxine blue (8-oxo-5-p-diethylaminophenylimino-5,8-dihydroquinoline)



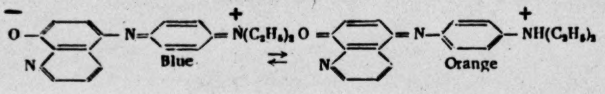
Simultaneously, apparently a byproduct is formed – 8-oxo-7-p-diethylaminophenylimino-5,8-dihydroquinoline. For purification, the mixture is subjected to chromatographic separation on an Al_2O_3 column. The indicator passes through the column, while the by-product is held in the upper third of the layer; yield 67.0%.

Oxine blue has good indicator properties. The visible transition change for the indicator color, established with the aid of a series of buffer solutions and potentiometrically, was found to be 3.90-5.50 (4.70 pH).

The indicator shows a clear-cut color change: in acid solution it has bright orange color, while in alkali solution it is blue. It has been established that the salt and temperature effects for oxine blue are insignificant. Comparative titration of a strong acid with a weak base using oxine blue and methyl orange respectively as indicators, and also titration with phenolphthalein gave practically identical results.

Indicator solution is prepared by dissolving 0.25 g of oxine blue in C_2H_5OH. 4-5 drops of this solution in 100 ml of test solution are sufficient to give indicator properties.

The mechanism of the color change can be represented as a change from an inner-ionoid form (blue color) to an ionic acid form (orange color).



The author wishes to express his thanks to Prof. A. V. Kirsanov on whose initiative, and under whose direction this work was carried out.

SUMMARY

The synthesis of oxine blue (8-oxo-5-p-diethylaminophenylimino-5,8-dihydroquinoline), which has good indicator properties, is described. The transition change for the indicator is at a pH of 3.90-5.00.

Received June 17, 1954

LITERATURE CITED

[1] Yu. V. Karyakin, "Acid Base Indicators", State Chem. Press, 1951.

DETECTION OF LEAD IN ORES BY THE TRITURATION METHOD

E. P. Ozhigov, M. A. Rafienko, and L. K. Ivanenko

Far-Eastern Branch of the USSR Academy of Sciences

Published methods [1-5], for detecting lead are not specific enough and require preliminary separation of lead from interfering elements. Recently an improved method for detecting lead has been suggested which is based on trituration of small amounts of its salts or ores first with potassium bisulfate, and subsequently with potassium iodide. When lead is present the mixture is colored yellow. Heating the triturated mixture speeds up appearance of the color. On treating the mixture with a drop of water, color intensity increases sharply. Of all reactions for lead based on the trituration method, the reaction with potassium iodide is the most suitable and reliable [6].

This method of trituration with KI has been checked on two different types of complex ores from the Primorsky deposits; results are described in the present communication.

Type A. A polymetallic ore containing up to 22 elements including SiO_2, Fe, Mn, Al, Ca, Mg, Pb, Zn, Bi, Cu and rare elements. Lead is chiefly in the form of the sulfide (lead content $> 1\%$).

Type B. A complex ore, containing fluorite as the major component; upwards of 40 different elements are contained in it including: Ca, F, Al, Fe, Mg, Zn, Sn, Sb, B and rare elements. Lead is in the form of the sulfide in this ore also (lead content – hundredths of a percent). The color of the ore of both types varies from light grey to dark brown.

Tests showed that detection of lead without heating is only possible for Type A ores. The reaction sensitivity in this case is not high. In order to determine the sensitivity of the method, test samples with a known lead content were successively diluted with amorphous silicic acid, and lead detected in the mixtures obtained. As an example, we have given in Table 1 the results for lead detection in one of the Type A ore samples.

TABLE 1

Ratio of ore to SiO_2 in mg		Pb content in %	Color after trituration
Ore	SiO_2		
5	—	17.4	Yellow
2.5	2.5	8.7	Yellow
1	4	3.4	Light yellow
0.5	4.5	1.7	Light yellow
0.25	5.75	0.35	Light yellow
0.12	4.88	0.42	Just observable traces
0.06	4.94	0.21	Not observed

Since the sensitivity of the method was not sufficient without heating, in a subsequent series of tests, the mixture, after trituration was heated for 1-2 minutes on an electric hot plate. Tests showed that it is best to add several drops of water, not just one. In order to lower the lead content in individual samples, the latter were diluted with amorphous silicic acid. Test samples which were mixed with silicic acid are designated in Table 2 with an asterisk.

The color intensity of the reaction product is linearly related to the lead content of the ore. The method permits determination of 0.0002% Pb, the sensitivity of the method is 200 times that of lead detection in solution with the help of K_2CrO_4. (According to the results of V. A. Nazarenko and N. S. Poluetkov [5], sensitivity of the detection of PbS in admixture with Pyrites amounts to 0.04%).

TABLE 2

Lead content		Ore type	Color after trituration
Percent or part of a percent	in %		
1% and over	22.64; 17.40; 15.90 14.70; 8.70; 11.70	A	Intensely yellow with a brownish shade
tenths of a %	0.84*; 0.78*; 0.65* 0.55*	A	Intense yellow, sometimes with a brownish shade
hundredths of a %	0.08*; 0.07*; 0.06*; 0.05*	A	Yellow
	0.052; 0.076; 0.021 0.031; 0.024	B	
thousandths and ten thousandths of a %	0.005*; 0.002*; 0.001* 0.0008*; 0.0002*	B	Light yellow

Thus detection of lead by means of trituration with KI followed by heating is highly specific and sensitive. The reaction can be used for detection of lead not only in minerals and concentrates of lead, but also for the analysis of complex polymetallic and fluorite ores containing a large number of various elements.

Received February 11, 1955

LITERATURE CITED

[1] V. A. Zilbermints, "Textbook and Tables for Determination of Minerals", Gen. Sci. Tech. Press, 1936, p. 34.

[2] H. Leitmeir and F. Feigl, Mineral u. petrog. Mitt., Abt. A, 47, 313 (1936); C. 1936, II, 1394.

[3] J. A Watson, Mineralog. Mag., 24, 21 (1935).

[4] P. West and L. Smith, J. Chem. Education 17, 139 (1940).

[5] V. A. Nazarenko and N. S. Poluetkov, "Semi-Micro Chemical Analysis of Minerals and Ores", State Chem. Press, 1950.

[6] P. M. Isakov, "Qualitative Analysis of Ores and Minerals by the Method of Powder Trituration", State Geol. Press, Moscow, 1953.

DETECTION OF FLUORINE IN MINERALS AND ORES BY A TRITURATION METHOD

E. P. Ozhigov[*]

Far-Eastern Branch of the USSR Academy of Sciences

Fluorine in minerals is detected by etching of glass [1], or by the formation of volatile SiF_4 and its hydrolysis in a "suspended" water drop [2], by decolorization by means of the fluoride ion of red zirconium-alizarin lake [3], or the yellow-orange peroxide compound of titanium [4].

No methods have been published for the detection of fluorine by a trituration method [5]. The present communication is an attempt to fill this gap.

For the qualitative analysis of ores and minerals for fluorine by a trituration method, we used decolorization of ferric thiocyanate, which is used for the quantitative determination of fluorine in natural waters [6]. For this purpose the salt or mineral is triturated with $KHSO_4$, after which a little $FeCl_3$ is added, followed by 2-3 crystals of KSCN or NH_4SCN. Addition of small amounts of water speed the decolorization of thiocyanates. The reaction is very sensitive, and even insignificant amounts of fluorine decolorize ferric thiocyanate obtained by triturating 5-6 mg of $FeCl_3$ with 8 mg of KSCN. Table 1 contains results on the detection of fluorine in fluorides of second group metals. Lowering of the fluoride content was carried out by "dilution" with amorphous silicic acid.

TABLE 1

Salts	Decolorization of $Fe(SCN)_3$ for different fluoride contents (in %)				
	100	10	1.0	0.1	0.01
CaF_2	× × ×[*]	× × ×	× ×	× ×	× ×
CaF_2 (Mineral)	× × ×	× × ×	× ×	× ×	× ×
SrF_2	× ×	× ×	× ×	× ×	× ×
BaF_2	×	×	×	×	×

[*] Decolorization: × × × on prolonged trituration; × × for a short duration of trituration; × for insignificant duration of trituration.

Decolorization is most difficult to carry out in the case of calcium fluoride; decolorization is least difficult when the fluoride is that of barium; this, presumably is connected with the energy of the crystalling lattices of these salts.

The second series of tests were carried out with an ore from another Primorsky deposit; this ore contained significant amounts of fluorite and Fe, Al, Mg, Zn, Sn, and Pb as impurities.

---

[*] M. A. Rafienko and A. Ya. Vinogradova took part in the work.

TABLE 2

Fluorine content In parts %	In %				Color of ferric thiocyanate
Tens	35.0	34.00	33.00	30.76	disappears
Units	3.5	3.4	3.3	3.08	"
Tenths	0.35	0.34	0.33	0.31	"
Hundredths	0.035	0.034	0.033	0.031	remains a hardly distinguishable rose color

Preliminary tests showed that a large amount of sulfide sulfur can lead to decolorization of ferric thiocyanate during trituration of the ore with $KHSO_4$. In this case it is best to use a mixture of ammonium salts [5]. Table 2 contains results for detection of fluorine in this ore. Starting at one percent, the ore was diluted with amorphous silicic acid.

The reaction suggested is fairly sensitive and specific*. It should be pointed out that the method described by I. M. Isakov for detection of ferric oxide based on trituration of the mixture with KSCN or NH_4SCN is not applicable to ores containing fluorine.

Received October 28, 1954

LITERATURE CITED

[1] V. A. Zilbermints, "Textbook and Tables for Determination of Minerals", 1936, p. 34.

[2] V. Gillebrand and G. Lendel, "Practical Textbook on Inorganic Analysis", Moscow, 1935, p. 640.

[3] V. A. Nazarenko and N. S. Poluetkov, "Semi-Micro Chemical Analysis of Minerals and Ores" State Chem. Press, 1950, p. 153.

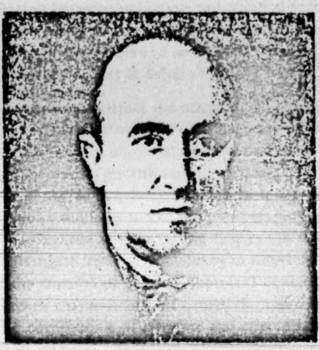
[4] N. I. Blok, "Qualitative Chemical Analysis" State Sci. Tech. Press Chem. Lit. Moscow-Leningrad, 1952, pp. 152, 542.

[5] P. M. Isakov, "Qualitative Analysis of Ores and Minerals by the Powder Trituration Method", State Geol. Press, Moscow, 1953.

[6] "Short Textbook on the Chemical Analysis of Water under Experimental Conditions" Edited by P. A. Kaminsky, USSR Acad. Sci. Press, Moscow-Leningrad, 1946.

---

* The phosphate ion, gives a yellow-white precipitate of the phosphate $FePO_4$ [4], when the reaction is carried out in aqueous solution. On trituration of reagents with phosphates, decolorization of thiocyanates is not observed, since, apparently, iron phosphate is not formed under these conditions. Addition of water leads to a breakdown of the thiocyanate and to the separation of a precipitate of a light-yellow color which differs from K_3FeF_6.



ANATOLY KIPRILOVICH BABKO

(On His Fiftieth Birthday)

On the 15th of October 1955 Anatoly Kiprilovich Babko celebrated his fiftieth birthday, and, at the same time completed 25 years of scientific and teaching work; he is an outstanding Soviet chemist, a Corresponding Member of the Ukrainian SSR Academy of Sciences, a doctor of chemical sciences, and a professor.

A. K. Babko is well known as a scientist, working most successfully in the field of theoretical and practical analytical chemistry and the chemistry of complex compounds, as a skillful research worker, and a first class teacher. After completing his course in the Chemistry Faculty of Kiev Polytechnical Institute in 1927, he stayed on in the analytical section as an assistant, and at the same time studied for a higher degree under the direction of Professor N. A. Tananaev, who Babko regards as his teacher. In the last 10–15 years, a large amount of his work was carried out in conjunction with several of his pupils and coworkers.

Since 1931 Babko has been a lecturer in the Chemistry Faculty of Kiev Technological Institute of the Food Industry, and from 1934, a lecturer in the Department of Analytical Chemistry of Kiev State University. Since that time Babko has also carried out work in the Ukrainian Academy of Sciences.

In 1940 Babko defended his thesis for a doctorate; this thesis was fundamental work devoted to the equilibrium of complex-formation in aqueous solution. The original ideas on which this work was developed served as a basis for the further development of methods of physico-chemical analysis of complexes in solution–a field which he has successfully developed right up to the present time.

Since 1941 Babko has been the head of the Laboratory of Analytical Chemistry of the Institute of General and Inorganic Chemistry of the Ukrainian Academy of Sciences. In 1943 he was made a professor, while in 1944 he became the head of the Chair of Analytical Chemistry in Kiev State University; in 1948 he was made a Corresponding Member of the Ukrainian Academy of Sciences.

The scientific interests of Babko are wide and multifarious. Mention may be made of the following fields in which his scientific activity has led to particularly fruitful results: general questions of analytical chemistry; methods for the analysis of various materials; the use of complex compounds in colorimetry; and the chemistry of complex compounds.

From his early work in the field of general analytical chemistry, of particular interest is his derivation of a formula in 1935 for calculating the solubility of precipitates—salts of polybasic acids during their interaction with hydrogen ions, and also in the absence, and in the presence, respectively of excess of each of the precipitants. In the same year he published an article on the effect of pH on oxidation-reduction potentials; the general physico-chemical characteristics of the relation between oxidation-reduction processes and the acidity of the solution are also considered. Subsequently, a large amount of the work he carried out was devoted to the study of complex compounds. A study of alumino-silicate complexes showed how wrong many of the theories in vogue at the time were, with respect to the behavior of these complexs in solution.

At that time complex compounds started to attract the attention of analytical chemists, in view of the numerous possibilities they showed for use as precipitants, "masking" agents, colored compounds, etc. Nevertheless, despite the interest in these compounds, there were no clearly formulated ideas re the nature of dissociation, or about the methods for studying complex-formation equilibrium in solution. Individual methods which were occasionally useful had been suggested, such as the Abegg-Bodlender method, and the Ostromyslensky-Job method. Nevertheless when it came to applying these methods to the study of complex-formation in solution, there was much that was not clear. Babko must be credited with being the first in the Soviet Union to start a systematic investigation, on the basis of a physico-chemical study of complexes in solution by the light absorption method. In the course of this work he widely used the method of physico-chemical analysis. He demonstrated the importance of the dissociation constant as an important characteristic of equilibrium in solution, developed the general position re step-wise dissociation, and ionic components of systems; and critically studied methods for determining the composition of complexes directly in solution. This work which continued over many years has now all been brought together in a monograph "The Physico-Chemical Analysis of Complex Compounds in Solution" (Acad. Sci. Press Ukrainian SSR, 1955).

From the investigations carried out by Babko to devlop methods of chemical analysis for practical purposes, use of the following types of reactions may be noted, e.g.,acid-base processes have been used for developing a colorimetric method of determining sodium carbonate in bicarbonate, volumetric methods of determining silicic acid, titration methods for silico fluorides, the lime method of determining alkaline metals in silicates. In the field of oxidation-reduction processes one should mention Babko's work on the use of electrolytic metals as solid reducing agents (1937). He developed the bismuth reducer, which is included in a State Specification for analysis of iron ores. A reducting buret is described for the rapid and simple preparation of trivalent titanium solutions.

Of great importance is his work on the physico-chemical basis of colorimetric methods of analysis, on the application of organic reagents, and the scientific foundation of the choice of optimum conditions for carrying out analytical determinations. He has derived equations relating formal deviations from Beer's law, the instability constant of the colored complex, and the concentrations of reactants. A vast amount of work has been carried out by him on colored thiocyanate complexes, on the salicylate and pyrocatechinate complexes of many metals and on dithizonates, dimethylglyoximates, and other complexes. This work, together with published results, served as a basis for the development of the fundamental precepts of colorimetric analysis. In 1951, in conjunction with A.T. Pilipenko, he published a book "Colorimetric Analysis," in which recommended methods of colorimetric analysis were given a serious fundamental basis.

In recent years Babko and his coworkers have been working on the analytical chemistry of rare metals, colorimetric methods of determining traces of non-metals, and determination of micro amounts of impurities in heat resistant alloys etc.

During his years of scientific activity Babko and his coworkers have carried out more than 125 projects which are a contribution to the development of analytical chemistry, chemical control of production, and the chemistry of complex compounds. All this work represents a new page in the theory of analytical chemistry and in the theory and practice of physico-chemical analysis of complexes in solution.

Babko has devoted a lot of his energies to training new cadres of Soviet scientists. Babko's lectures on qualitative and quantitative analysis, on the methods of physico-chemical analysis, and his special courses on the theoretical basis of analytical chemistry are very popular with the students at Kiev State University. His wide knowledge, the ability to impart his knowledge to others, his mastery of experimental technique, the demands he makes on himself, his coworkers and his pupils, have enabled Babko to create a school of analytical chemists.

His activity extends well beyond the confines of scientific research in the laboratory and his lectures. He is well known to Soviet chemists as a lecturer at many chemical meetings and conferences, and as a consultant on various questions of analytical chemistry and chemical control of production. While working in Kiev, A. K. Babko represents with honour Ukrainian Chemists, he has successfully developed chemical science together with other brotherly republics of the USSR.

For his successfull scientific and scientific-organization work Babko has been awarded the Order of Lenin, The Mark of Honour and the Medal "For Glorious Work in the Great War 1941—1945."

At the present time, Babko, a leading Soviet scientist, is energetically and with inspiration continuing his creative scientific, teaching, and general activity.

BLANK
PAGE

CHRONICLE

CONFERENCE HELD IN GORKY STATE UNIVERSITY ON THE APPLICATION OF LABELED ATOMS IN CHEMISTRY

During 21-24th of December 1955 a conference on the use of labeled atoms in chemistry organized by Gorky State University, was held; more than 200 participated in this conference, including scientific workers from Moscow, Leningrad, Kazan and other cities, factory workers, and teachers and scientific workers from Gorky and district. 34 papers were delivered at three plenary and six section meetings.

Opening the conference, the rector of the University V. I. Shuirokov noted that the application of labeled atoms is one of the most important fields of the use of atomic energy for peaceful purposes, and pointed out that Gorky State University has accumulated considerable experience in the application of radioactive and stable isotopes in chemical research. I. A. Korshunov and I. M. Korenman in a plenary session gave a detailed review of fundamental research carried out with labeled atoms.

A group of reports in the section of radiochemistry and physical chemistry was devoted to the study of the application of the isotope effect to velocity constants of the hydrolysis of several carboxylic esters (I. A. Korshunov, N. F. Novtorov), to the vapor pressure of multi-atomic molecules (G. G. Devyatykh), to the mutual solubility of liquid deutero compounds (I.B.Rabinovich, V. D. Fedorova). The reports of N. N. Tunitsky (The Karpov Institute of Chemistry, Moscow), B. P. Nikolsky (Leningrad University), G. G. Devyatykh, V. A. Shushunov, B. Z. Torlin (Moscow), A. D. Zorin, N. I. Nikolaev, M. K. Shchennikova, B. G. Zateev were devoted to isotope separation. Results of studies on the state of radioactive phosphorus in targets after irradiation with neutrons were given in the reports of I. A. Korshunov and A. I. Shafiev. Investigation of the state of niobium and zirconium in solution was the object of the report of V. I. Paramonova, A. S. Voevodsky, and V. V. Kolychev (Leningrad University). M. B. Neuman and V. B. Miller's report touched on the use of labeled atoms for studying the mechanism of complex reactions.

A. M. Petrov reported his findings on the adsorption of metals from solutions of their salts by various materials; while B. M. Noskov read a report on the study of diffusion and interatomic reactions in crystals. I. A. Korshunov and N. F. Novotorov reported the synthesis of organic compounds labeled with a radioactive carbon isotope.

One of the sessions on analytical chemistry was devoted to a consideration of coprecipitation. In the report of I. M. Korenman, A. A. Tumanov, Z. I. Glazunov, Z. V. Krainova, and M. N. Baryshnikova, information was given on the study of the mechanism of coprecipitation with precipitates, obtained by the action of organic precipitants (hydroxyquinoline, anthranilic acid, antipyrine, and pyridine). This question was also touched upon in the report of I. M. Korenman, P. A. Ganichev, and G. A. Shatalina (precipitation of picrates and dipicrylaminates). I. M. Korenman and M. N. Baryshnikov, communicated on the coprecipitation of micro-amounts of zinc, cadmium, and mercury with a precipitate of anthranilic acid. N. A. Rudnev (Moscow, Institute of Geochemistry and Analytical Chemistry) communicated on the elimination, or diminution of coprecipitation, of a number of cations with sulfide precipitates, on addition of surface active agents.

The reports of I. M. Korenman, F. R. Sheyanova, and V. V. Korolikhin touched on the use of radioactive indicators for studying extraction of inner complex compounds. I. M. Korenman and F. R. Sheyanova's report was devoted to the use of non-isotope indicators for determining the solubility of certain salts. Determination of the solubility of carbon dioxide by the method of isotope dilution was the theme of the report given by M. K. Shchennikova, G. G Devyatikh, and I. A. Korshunov. I. M. Koreman and E. I. Zorin reported a rapid method for determining cadmium by measuring its natural radioactivity. N P. Drozdov and A. N. Popov's report touched on the use of radio sulfur for determining the content of sulfonate groups in sulfonated coal. N. P. Drozdov and E. I. Paveleva's report was devoted to the radiographical method of analysis.

In the final plenary session, reports by I A. Korenman, N. F Novotorov, and A. I. Shafiev were heard on methods of determining the activity of solid and liquid preparations, and also on methods of determining the activity of compounds containing radioactive carbon. The question of safety during working with labeled atoms was discussed in the report of A. M. Petrov. Practically all the reports led to lively discussion.

In this short note it is impossible to give full justice to each of the reports; nevertheless, the list of reports given above show what a large number of questions were discussed at the conference, which were connected with the use of radioactive indicators in chemistry.

The conference adopted a resolution approving the initiative of the Gorky State University in calling this conference; the need for calling similar conferences periodically is pointed out. The resolution also notes the work carried out in Gorky State University on the use of labeled atoms in chemistry. The resolution also recommends that chemical laboratories and industrial enterprises in Gorky should use labeled atoms on a wider scale in their work.

I. M Korenman

ANNOUNCEMENT

The Commission on Analytical Chemistry of the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences, are getting ready to print a collection of articles on spectrophotometric and colorimetric method of analysis, amounting to about 30 pages compiled from material given at the All-Union Conference held on the 15–17 December 1955.

The collection will include review articles devoted to the present position of analysis on light absorption (descriptions of current analytical methods, apparatus used, and their prospective development), and also original articles on the theory and practical application of spectorphotometric and colorimetric methods of analysis for studying the processes of complex formation in solution, establishing molecular structure, determining the composition and dissociation constants of complex compounds, and identification of materials from their absorption spectra.

The collection includes articles devoted to determination of small concentrations of elements in pure metals and alloys, in natural water, etc., and also papers on the determination of organic compounds using the infra-red.

A number of articles are devoted to a description of practical methods of analysis and the apparatus used, and also to descriptions of improvements to apparatus used in the methods.

It is proposed to publish this collection in the first quarter of 1957.

BLANK
PAGE

METHODS OF ISOLATING CARRIER FREE RADIOACTIVE ISOTOPES

PART I. PREPARATION OF RADIOCHEMICALLY PURE ThB AND ThC

N. P. Rudenko

Second Physical Institute for Scientific Research, Moscow State University

Having come up against the necessity of separating ThB and ThC, and preparing radiochemically pure preparations of these isotopes free from carriers in 1948, we were compelled, in the absence of a rapid and reliable method, to develop a method of separating the isotopes mentioned.

The basis of the method developed for the separation of ThB (Pb^{212}) and ThC (Bi^{212}) was determination of microamounts of bismuth and lead with dithizone (diphenylthiocarbazone). The latter arose as the result of the discovery by Fischer [1-3], of a sensitive reaction between dithizone and a large number of chemical elements. The method was developed as a quantitative one for lead by Fischer and Leopold [4], and was further improved, and also applied for the individual determination of bismuth and lead, both by them [5, 6] and by a number of other chemists [7-36]. This method has been successfully used for the determination of bismuth and lead in amounts of the order of a few micrograms in biological materials (urine, blood, preserves, etc.), water, air and minerals. Bismuth and lead, under certain conditions, form intensely colored inner complex salts with dithizone, which are soluble in chloroform, carbon tetrachloride, carbon disulfide, etc.

Determination of micro amounts of bismuth and lead, for example in biological materials, after ashing and dissolving the ash, reduces to extraction of bismuth and lead dithizonates by chloroform from a weakly alkaline solution (pH 8.5-9.0), containing 1% potassium cyanide. Extraction was carried out by shaking the aqueous solution with aliquots of a chloroform solution of dithizone, until a fresh portion of the organic solvent did not change the color characteristic of the dithizone solution, on shaking. The united chloroform extracts were shaken with water to remove the cyanide; bismuth and lead which may partially transfer into the aqueous layer during this process were re-extracted with a chloroform solution of dithizone.

Bismuth and lead were transferred to the aqueous phase from the organic solvent by shaking with 0.15 N nitric acid; by selective extraction of the aqueous phase at a pH of 2.5 - 3.0, bismuth dithizonate was then separated from the lead compound.

Despite the existence of such a simple analytical method, during studies of the radioactive isotopes of bismuth and lead, these metals have been separated from each other by methods which are far more complex, take a longer time to carry out, and, as a rule, necessitate addition of carriers. Thus, Fajans and Foigt [37], separated radioactive bismuth by precipitation with hydrogen sulfide, by hydrolysis of solutions of bismuth salts, and by reduction of ionic bismuth to the metallic state with formaldehyde or sodium stannite. Templeton, Howland, and Perlman [38], after addition of an inactive carrier separated bismuth as the iodate, while lead was separated as the sulfate or chromate, and only in one instance were lead and bismuth separated by extraction. Alburger and Friedlander [39], used a very complicated method which included two precipitations, electrolytic and electrochemical separation, and extraction. Campbell and Nelson [41], and Fred and coworkers [42], used an ion-exchange method. Grace and Presscott [40], resorted to precipitation of bismuth oxychloride for separating radioactive bismuth and lead. Spiess [43], used precipitation of bismuth thionalidate, and electrochemical separation of bismuth with metallic nickel.

EXPERIMENTAL

A radio-thorium preparation served as the source of the radioactive isotopes of lead ThB, and bismuth ThC.

A metal foil connected to the negative pole of a battery was placed in the thoron atmosphere of this preparation, and the daughter products of the thoron captured on it. Apart from the ThB and ThC required for the research, the active precipitate also contained another series of radioactive isotopes; thanks however to the short half life period of ThA (Po^{216}), this decomposed in a fraction of a minute, while ThC' (Po^{212}), and ThC" (Tl^{208}) rapidly (a fraction of a second and 14.25 minutes respectively) came into equilibrium with ThC.

Two variants were worked out for separating ThB and ThC.

A. Separation of ThB and ThC without using a carrier. The radioactive deposit, collected from a gold or aluminum foil, was dissolved in concentrated nitric acid; the solution was then evaporated on a water bath after removal of the foil. After the container had been allowed to cool, the invisible residue was dissolved in 2 ml of a buffer mixture with a pH of 2.60 to 3.00 (an acetate buffer solution with a concentration of 0.02 for the acetate ion). Dissolution of the residue which is too small to be weighed does not change the buffer. This solution was transferred to a separating funnel and shaken for 3 minutes** with an equal volume of a 0.01% solution of dithizone in chloroform. After settling, the chloroform layer was poured into another separating funnel and washed twice with equal volumes of a buffer mixture with the same pH value. If a dry preparation is required, and excess dithizone can be tolerated, then the chloroform layer can be carefully evaporated to dryness; otherwise, the chloroform solution is shaken with 1 N hydrochloric acid into which the ThC transfers completely. ThC is practically completely separated from ThB after three extractions; when the fourth extract proved to be slightly active, all the activity transferred to the buffer wash liquid, showing that it was ThB.

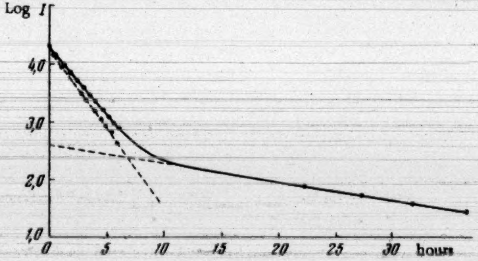


Figure 1. Change in activity of the unwashed chloroform phase.*

---

* The activity of equal volumes of the chloroform and aqueous phases was determined after evaporation in standard glass beakers. Measurement of the preparations, which gave more than 5,000 counts per minute for the geometry accepted for measurement, was also carried out for another geometry (at a greater distance from the counter), and was afterwards recalculated in terms of the standard.

** Kozlyaeva [23], established that it is sufficient to shake an aqueous solution containing lead, with a chloroform solution of dithizone for 10-20 seconds. Sandell [35], p. 174, recommends shaking for 15 seconds, although he indicates [35], p. 425, that at pH 2, extraction proceeds slowly. Taking into account the latter assertion, we shook the solutions for three minutes, though we were convinced that equilibrium between the phases is achieved in a shorter time than three minutes.

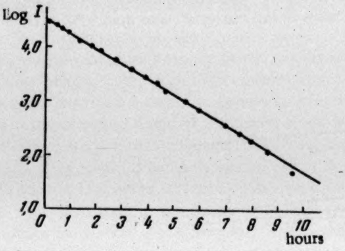


Figure 2. Change in activity of the chloroform phase washed with buffer solution.*

As was shown experimentally, just one extraction was not sufficient to extract all the ThC; moreover, in individual experiments, the evaporated chloroform extract proved to be active 20-30 hours after separation (Fig. 1). This testifies to a partial transfer of ThB into the chloroform layer, and to the necessity of washing the latter. It was established that one wash with an acetate buffer of the same pH value was quite sufficient for complete removal of ThB from the organic phase (Fig. 2). A second wash liquor usually remained inactive. During washing, negligible amounts of ThC are extracted with the ThB. Proof of this is given by the position of the break on the curve in Fig. 3, and on Curves 2, 5, and 8 of Fig. 4, and the earlier onset of radioactive equilibrium (2.8-3.5 hours instead of 3.97) after washing.

Results of one of the experiments on the separation of ThB and ThC at a pH of 2.90, without using a carrier, are presented in Fig. 4. Similar results were obtained in other experiments in which the pH was varied from 2.70 to 3.03. Removal of ThC was effected by a threefold extraction. Each chloroform layer was twice washed with an equal volume of buffer solution with the same pH value. Results of activity measurements on the preparation are given in Fig. 4 by the following lines: ThC (chloroform phase, twice washed with buffer solution) – by lines 1, 4, 7 (first, second, third, extraction); the first wash liquor – by lines 2, 5, and 8; the second wash liquor – by points 3, 6, 9 (the result of measurements after 1 hour was on the level of the background); the aqueous solution after three extractions of ThC – by line 10.

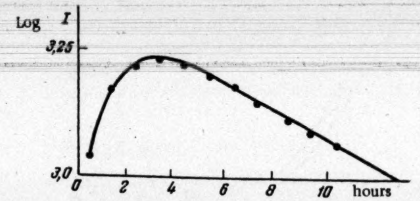


Figure 3. Change in activity of the wash liquor.

Results of a similar test are presented in Fig. 5; in this case, washing was carried out with water, and not with a buffer solution (the legends are the same as for Fig. 4); the use of water along is the reason for the washing out of large amounts of ThC from the chloroform phase, and the incomplete washing out of ThB (compare Curves 2, 5, and 8 of Figs. 4 and 5 respectively). The Curves 1, 4, and 7, of Fig. 5 deviate from linearity which indicates contamination of the chloroform phase by some ThB after just one wash with water.

---

* The original points on Curves 2-5 are plotted at distances from the ordinate which correspond to the time which has elapsed between separation and measurement.

On the basis of these diagrams the following conclusions can be drawn:

1. A one stage extraction of the radioactive bismuth isotope ThC as the dithizonate (taking into account accumulation of ThC between two successive extractions) leads to extraction of more than 80% of the bismuth under the conditions outlined above.

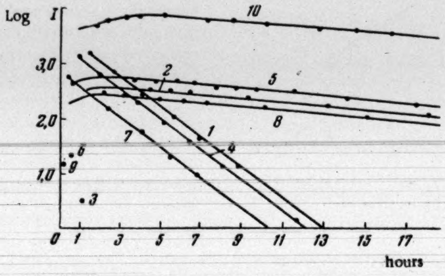


Figure 4. (Explanation in text)[*]

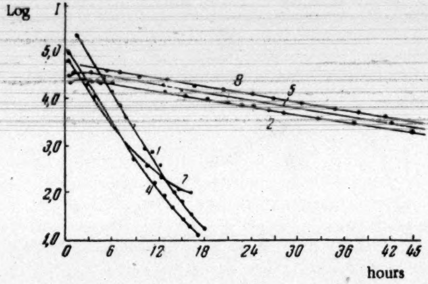


Figure 5. (Explanation in text)

2. The percentage of the radioactive isotope of lead ThB which transfers under these same conditions into the chloroform, amounts to 3.5% on an average.

3. For removal of lead dithizonate from the organic solvent, it is essential, but quite sufficient, to wash once with an equal volume of a buffer solution with the same pH value (2.6-3.0).

---

[*] No corrections are made to the results of activity measurements for differences in the efficiency of the β-ray counter for the isotopes ThB, ThC, and ThC*, or for the fact that β-radiation accompanies only 66.3% of ThC nuclear decompositions.

4. The percentage extraction of ThC, the radioactive isotope of bismuth, from the organic layer amounts to ~ 2% for one extraction.

B. Variant involving the use of a carrier. A lead plate may be used in this variant for collecting the radioactive deposit. Solution of the radioactive deposit of thoron from the plate is carried out by gentle heating in the minimum amount of nitric acid (1:1). The nitric solution is transferred into another beaker and evaporated almost to dryness on a water bath, with 0.01 mg of bismuth as the nitrate. The residue is transferred to a separating funnel, made from a tube used for colorimetric determination of pH; the few drops of dilute nitric acid used for washing the beaker are also added to this funnel. The solution in the separating funnel is partially neutralized with ammonia to a pH of 2.9-3.1, using an indicator, the color of the test solution being matched up to a solution in an ampoule with a pH of 3.0 on a specially prepared scale. An equal volume of a 0.01% solution of dithizone in chloroform is then introduced into the funnel, and extraction carried out as described above. Results are similar to those given in Fig. 4.

Whichever variant is used, the method is fairly rapid; by means of this method an appreciable amount of ThC preparation was obtained, and careful study of the radiation from the preparations showed the absence of ThB in them. The work of Bouissieres and Ferradini, who used extraction of the dithizonates of RaD, RaE, and RaF with chloroform for their separation, was published in 1950 [44].

SUMMARY

A rapid extraction method for separating ThB and ThC has been developed which allows preparations of these radioactive isotopes to be obtained in a radiochemically pure state, both with and without the use of carriers.

LITERATURE CITED

[1] H. Fischer, Wiss. Verōffentl. Siemens-Konzern 4, 158 (1925); cited in Chemical Abstracts 20, 3660 (1926).

[2] H. Fischer, ibid. 6 [2], 147 (1928); cited in Chemical Abstracts 23, 1364 (1929).

[3] H. Fischer, Z. angew. Chem. 42, 1025 (1929).

[4] H. Fischer and G. Leopoldi, Wiss. Verōffentl. Siemens-Konzern, 12, 44 (1933); cited in Chemical Abstracts 27, 3418 (1933).

[5] H. Fischer and G. Leopoldi, Z. angew. Chem. 47, 90 (1934).

[6] H. Fischer and G. Leopoldi, Z. anal. Chem. 119, 161 (1940).

[7] L. Haddock, Analyst 59, 163 (1934).

[8] H. Wichmann, C. Murray, M. Harris, P. Clifford, J. Longhrey and F. Vorhes, J. Assoc. Offic. Agr. Chemists 17, 103 (1934); cited in Chemical Abstracts 28, 2070 (1934).

[9] H. Wichmann and P. Clifford, ibid. 18, 315 (1935); cited in Chemical Abstracts 29, 4839 (1935).

[10] E. Wilkins, C. Willoughby, E. Kraemer and F. Smith, Ind. Eng. Chem.,Anal. Ed. 7, 33 (1935).

[11] C. Willoughby, E. Wilkins and E. Kraemer, ibid. 7, 285 (1935).

[12] A. V. Evlanova, J. Appl. Chem. 9, 1690 (1936).

[13] P. Clifford and H. Wichmann, J. Assoc. Offic. Agr. Chemists 19, 130 (1936); cited in Chemical Abstracts 30, 2877 (1936).

[14] P. Clifford, ibid. 23, 307 (1940); cited in Chemical Abstracts, 34, 5187 (1940).

[15] D. Hubbard, Ind. Eng. Chem., Anal. Ed. 9, 493 (1937).

[16] G. A. Evlanov, Sci. Rpts. Plekhanov Inst. Nat. Econ. 1, 131 (1938).

[17] J. Perlman, J. Assoc. Offic. Agr. Chemists 20, 622 (1937); cited in Chemical Abstracts 32, 258 (1938).

[18] J. Perlman, Ind. Eng. Chem., Anal. Ed. 10, 134 (1938).

[19] H. Müller, Z. anal. Chem. 113, 161 (1938).

[20] V. M. Prikhniya, Factory Lab. 8, 283 (1939).

[21] D. Hubbard, Ind. Eng. Chem., Anal. Ed. 11, 343 (1939).

[22] C. Reith van Dijk, Chem. Weekblad 36, 341 (1939); 36, 343 (1939); cited in Chemical Abstracts 33, 7234 (1939).

[23] K. Bambach, Ind. Eng. Chem., Anal. Ed. 11, 400 (1939).

[24] H. Wichmann, ibid. 11, 66 (1939).

[25] T. N. Kozlyaeva, Trans. Chem. Lab. All Union Sci. Research Inst. Protection of Labor No. 3, 77 (1941).

[26] I. Kolthoff and E. Sandell, J. Am. Chem. Soc. 63, 1906 (1941).

[27] L. Biefeld and T. Patrick, Ind. Eng. Chem., Anal. Ed. 14, 275 (1942).

[28] K. Bambach and R. Burkey, ibid. 14, 904 (1942).

[29] A. K. Babko and A. T. Pilipenko, J. Anal. Chem. 1, 275 (1946).

[30] A. K. Babko and A. T. Pilipenko, ibid., 2, 33 (1947).

[31] H. Irwing and E. Butler, Anal. Chem. 25, 995 (1953).

[32] D. Elvidge and D. Carratt, ibid. 25, 995 (1953); R. Milton, ibid. 25, 995 (1953).

[33] S. Cooper and J. Hibbits, J. Am. Chem. Soc. 75, 5084 (1953).

[34] A. G. Karabash, J. Anal. Chem. 8, 140 (1953) (T. p. 159)* ; H. Irving and C. Bell, Nature 169, 756 (1952).

[35] E. Sandell, "Colorimetric Determination of Traces of Metals", State Chem. Press, 1949.

[36] A. K. Babko and A. T. Pilipenko, "Colorimetric Analysis", State Chem. Press, 1951.

[37] K. Fajans and A. Foigt, Phys. Rev. 60, 619 (1941).

[38] D. Templeton, J. Howland and I. Perlman, Phys. Rev. 72, 758, 766, 771 (1947).

[39] D. Alburger and G. Friedlander, Phys. Rev. 81, 523 (1951).

[40] M. Grace and J. Presscott, ibid. 84, 1059 (1951).

[41] E. Campbell and F. Nelson, ibid. 91, 499 (1953).

[42] M. Fred, F. Tompkins and R. Barnes, ibid. 92, 1324 (1953).

[43] F. Spiess, ibid. 94, 1292 (1954).

[44] G. Bouissieres and Ch. Ferradini, Anal. chim. Acta, 4, 610 (1950).

Received January 11, 1956

---

* T. p. = C. B. Translation pagination.

RAPID METHODS OF MICRO ELEMENTAL ANALYSIS

PART X* SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN, AND HALOGENS IN HALOGEN-CONTAINING ORGANIC COMPOUNDS

M. O. Korshun and N. S. Sheveleva

Institute of Elemental Organic Compounds, Academy of Sciences USSR, Moscow

In 1948 we demonstrated the possibility of carrying out simultaneous micro determination of carbon, hydrogen, and halogens [1], in halo-organic compounds. It was pointed out then that during pyrolytic combustion of organic materials containing halogens, in the absence of oxidizing and catalytic agents, even when a large excess of oxygen and a high temperature of the oxidizing zone is used ** (900-950°), the carbon is not quantitatively oxidized to CO_2; as a result, low and variable results were obtained for carbon. Only the presence of a platinum catalyst ensured complete oxidation of the products of thermal decomposition of these materials, and getting good results [2].

Nevertheless, other authors [3, 4] who determined carbon, hydrogen, and halogens by rapid combustion in an empty tube, observed quantitative oxidation of halo-organic compounds. Moreover, it was observed that at the temperature at which we formerly heated the silver (400-450°), although the halogens were quantitatively trapped, the silver very rapidly deteriorated and had to be changed often.

All these facts led us to study the temperature conditions for silver more carefully, and the reasons for incomplete oxidation of halo-organic materials under the conditions used for rapid pyrolytic combustion in an empty tube.

Temperature Conditions for Retention of Halogens by Silver

Results which have been published for the temperature at which silver should be heated in order to attain complete trapping of halogens, during elemental analysis of halo-organic compounds, are very contradictory. Some authors trap halogens by heating silver at 600-800° [3-6], while others heat it to 290-300° [7, 8]. Complete absorption of halogens also depends on the heated surface area of the silver. Thus, Colson [4], took a layer of granulated metallic silver 150 mm long. This amount of silver weighs 30 g and is only sufficient for 50 micro-determinations. The other authors mentioned above used silver netting, weighing from 6-12 g.

On the basis of six years experience on simultaneous determination of carbon, hydrogen, and halogens, it may be regarded as established that silver, at comparatively low temperatures, although it is capable of trapping halogens, all the same tarnishes, becomes covered by a thin film all over its surface, and loses its activity. As a result, the amount of silver which we normally use, is insufficient even for one analysis. On subsequent heating of the silver to a higher temperature (800°), the film disappears; in a matter of seconds, the surface resumes its usual luster, the silver again becomes active, while the weight of the apparatus remains unchanged. Determination of chlorine in butylchloral hydrate (Table 1), showed that even at 550-600°, silver quantitatively traps the halogen, and no film formation is observed. It may be postulated that even at lower temperatures (from 200-450°), the halogens, in the main, react with silver only on the surface, while the silver halide formed as a very fine film prevents further interaction between halogen and metallic silver; at higher temperatures, silver reacts in the mass. Accordingly, at 550-600°, considerably less silver is required for halogen absorption, and 2-3 mg is fully sufficient for carrying out 30-40 determinations of chlorine, bromine, and iodine. Usually, we use silver ribbon, foil, or netting, rolled into the forms of spirals 60-70 mm long; the silver is placed in a quartz apparatus connected via ground glass joints to the combustion tube.*

---

* Part IX, J. Anal. Chem. 11, 3 (1956) (C. B. translation p. 1).

** By the oxidation zone we mean that part of the combustion tube which is heated by the electric oven.

TABLE 1

Determination of Chlorine in Butylchloral Hydrate When Silver is Heated at Various Temperatures. Calculated: Cl 54.98 %.

Temperature in °C	Weight of sample in mg	Weight of Cl in mg	Amount found in % absolute	Temperature in °C	Weight of sample in mg	Weight of Cl in mg	Amount found in % absolute
200	7,135	1,778	24,92	460	5,958	3,130	52,54
220	7,290	1,905	26,13	480	6,088	3,216	52,83
320	5,497	1,260	22,92	500	6,807	3,708	54,48
320	6,418	1,550	24,15	550	5,908	3,270	55,24
440	5,290	2,586	48,89	600	6,908	3,795	54,94

Note: Combustion was carried out in a stream of O_2 passing through at the rate of 35-40 ml/minute; the length of the heated zone of the combustion tube was 10 cm, while the temperature was 950°; the length of the heated zone in the silver-containing apparatus was 10 cm.

Halogens were determined after combustion, by weighing the apparatus with the silver, in exactly the same way as for sulfur [9]. In order to improve cooling of the apparatus, we placed it on a long metallic block of the type shown in Fig. 1.

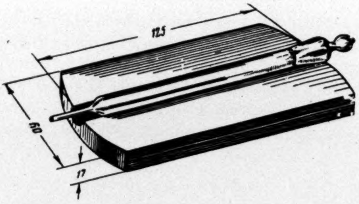


Figure 1. Metallic block.

---

* Silvered pumice or silica gel may be used instead of metallic silver.

As noted already, considerable difficulties in determining carbon by the rapid method in materials containing chlorine, bromine, and iodine, confronted us unexpectedly. Of the many compounds tested, the one which gave the lowest yield of carbon on combustion proved to be bromo-anthracene; instead of the expected theoretical value of 65.45%, we got values of 45-47% (Table 2). The length of the heated zone had no effect on the quantitative yield of carbon dioxide: similar low results were obtained for carbon when the combustion tube was heated with both a short oven 10 cm long, or with a longer oven 20-25 cm long.

TABLE 2

Determination of C and H Under Various Conditions of Pyrolytic Combustion

Test compound	Experiment No.	Whether contacts are present or not	Found in %		Difference in %	
			C	H	C	H
3,3,3,1-Tetrachloropropylene-1 $C_2H_2Cl_4$ C − 20.03; H − 1.12	1	No	13,99	1,32	− 6,04	+0,20
	2	»	11,82	1,26	− 8,29	+0,14
	3	Yes	20,32	1,22	+ 0,29	+0,10
	4	»	20,18	1,16	+ 0,15	+0,04
β-Chlorovinyl-n-chlorophenyliodonium hydrochloride $C_8H_6Cl_3I$ C − 28.64; H − 1.80	5	No	20,83	1,73	− 7,81	−0,07
	6	»	18,50	1,75	−10,14	−0,05
	7	Yes	28,40	1,67	− 0,24	−0,13
	8	»	28,44	1,64	− 0,20	−0,16
4-Bromo-4-methylpentene-2 $C_6H_{11}Br$ C−44.20; H−6.81	9	No	40,63	6,82	− 3,57	+0,01
	10	Yes	44,22	6,95	+ 0,02	+0,14
	11	»	44,33	6,91	+ 0,12	+0,06
Bromo-anthracene $C_{14}H_9Br$ C − 65.39; H − 3.53	12	No	47,58	3,72	−17,81	+0,19
	13	»	45,27	3,70	−20,12	+0,17
	14	Yes	65,45	3,69	+ 0,06	+0,16
	15*	No	65,31	3,61	− 0,08	+0,08
Hexachlorocyclohexane $C_6H_6Cl_6$ C − 24.74; H − 2.06	16	»	23,08	2,33	− 1,76	+0,27
	17	Yes	25,00	2,32	+ 0,26	+0,26
	18*	No	25,01	2,35	+ 0,27	+0,29
Bromonaphthalene $C_{10}H_7Br$ C−58.00; H−3.41	19	»	54,08	3,51	− 3,92	+0,10
	20	Yes	58,07	3,47	+ 0,07	+0,06
	21*	No	57,87	3,44	− 0,13	+0,14
	22**	»	57,78	3,52	− 0,22	+0,11
	23**	»	57,87	3,49	− 0,13	+0,08

---

* The temperature of the oxidizing zone in Experiments 15, 18, and 21 was 1100°.

** In Experiments 22 and 23, the silver was placed in the combustion tube as shown in Fig. 2.

On the assumption that the loss of carbon was the result of carbon monoxide formation, complete oxidation of which is prevented by the halogens present in the test material; we first of all carried out qualitative tests for CO in the gaseous products of combustion of bromo-napthalene issuing from the combustion tube, and actually found carbon monoxide. Next, we tried to determine CO quantitatively, and trap all the other products formed in order to make up the balance for the content of all elements present. In order to do this, bromine was trapped with silver at 550-600° in an apparatus connected via ground glass joints with the combustion tube [9]. This apparatus was then connected successively to the apparatus used for trapping water and carbon dioxide. This apparatus was followed by a tube containing cupric oxide heated to 800°, and a second apparatus filled with ascarite. From the increase in weight of this tube we got the amount of CO present in the form of CO_2. It is clear from the results given below that the total carbon obtained as CO_2 and CO, differs by only 0.2% from the theoretical value, while the sum of all the elements confirms the empirical formula of bromo-naphthalene. It may be assumed therefore that carbon monoxide is formed, and that this is responsible for carbon loss during pyrolytic combustion of halo-organic compounds.

TABLE 3

Halogen Determinations

Test compound	Weight taken in mg	Weight of halogen in mg	Weight of halogen in %		
			Found	Calculated	Difference
n-Chloroacetylguanine	4,705	0,720	15,30	15,57	—0,27
$C_7H_6O_2N_5Cl$	6,200	0,940	15,16		—0,41
Methyl-2-(3-chlorobicyclo) 2,2,1(heptene-5-yl) ketone	9,585	1,955	20,40	20,78	—0,38
$C_9H_{11}OCl$	5,005	1,025	20,48		—0,30
o-Nitrochlorobenzene	5,608	1,259	22,45	22,50	—0,05
$C_6H_4ClNO_2$	7,450	1,668	22,39		—0,11
2-β-Ethoxy-1-ethoxybromocyclohexane	4,670	1,495	32,00	31,82	+0,18
$C_6H_{19}O_2Br$	6,075	1,930	31,79		—0,03
Bromo-naphthalene	6,735	2,620	38,90	38,59	—0,31
$C_{10}H_7Br$	8,080	3,123	38,65		+0,06
3,5-Dichlorocyclopentene-1	3,885	2,020	51,99	51,78	+0,21
$C_5H_6Cl_2$	5,740	2,970	51,75		—0,05
Isobutyl-α-iodovinylketone	5,590	3,000	53,67	53,31	+0,36
$C_7H_{11}OI$	6,635	3,545	53,47		+0,16
Dibromoethylene	7,790	6,640	85,24	85,07	+0,17
$C_2H_4Br_2$	6,180	5,280	85,44		+0,06

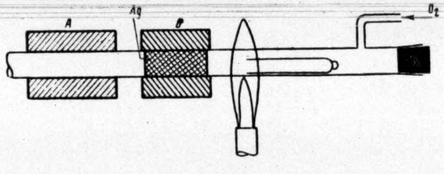


Figure 2. Electric ovens: A) 110 mm long at 900°; B) 60 mm long at 600°.

Combustion of Bromo-naphthalene

Found in mg	6,735	8,080
CO_2 in mg	14,100	15,787
CO in the form of CO_2 in mg	0,230	1,385
H_2O in mg	2,090	2,510
Br in mg	2,630	3,123

Found in %:		
C in the form of CO_2	57,13	53,32
C in the form of CO	0,93	4,68
C (total)	58,06	58,00
H	3,47	3,47
Br	38,90	38,65
Total	100,43	100,12

Calculated for $C_{10}H_7Br$ %: C 58.00; H 3.41; Br 38.59.

Subsequently, we carried out tests in which we trapped halogens directly with silver at 550-600° in the combustion tube (as shown in Fig. 2) with the aim of trapping the halogen immediately after decomposition of the material, i.e., before the products of thermal decomposition in admixture with oxygen fall into the oxidizing zone. In this case, correct results were obtained for carbon during combustion of bromo-naphthalene (Table 2).

Good results were obtained for carbon during the combustion of these same materials in the presence of a platinum catalyst heated to 900-950° (Table 2). We used platinum foil, netting, or wire rolled into spirals 4-5 cm long as catalysts.

In the light of knowledge derived from the present studies, it may be postulated that under the conditions of pyrolytic decomposition of halo-organic compounds, simpler halogen compounds or even radicals may appear

TABLE 4
Simultaneous Determination of Carbon, Hydrogen, and Halogens

Test material	Sample weight	CO_2	H_2O	Hal	Found (in %)			Difference (in %)		
	im mg				C	H	Hal	C	H	Hal
β-Endo-9,10-dihydroanthrol-chloramylvinylketone	9.083	25.930	5.660	0.942	77.91	6.85	10.37	−0.06	+0.01	−0.04
$C_{22}H_{23}OCl$. C − 77.97; H − 6.84; Cl − 10.41	11.100	31.769	6.900	1.183	78.11	6.96	10.66	+0.14	+0.12	+0.25
Benzodiglycin ethanolamine ether chlorohydrate *	6.285	11.375	3.390	0.710	49.37	6.04	11.30	−0.08	+0.30	+0.07
$C_{13}H_{18}O_4N_3Cl$. C − 49.45; H − 5.74; Cl − 11.23	7.175	12.960	3.820	0.810	49.30	5.95	11.21	−0.15	+0.21	+0.06
o-Nitrochlorobenzene *	5.870	9.910	1.426	1.330	46.07	2.72	22.66	+0.34	+0.16	+0.16
$C_6H_4ClNO_2$. C − 45.73; H − 2.56; Cl − 22.50	6.180	10.362	1.520	1.390	45.74	2.75	22.49	+0.01	+0.19	+0.02
Ethyl-γ-bromopropylcyclopentanone	7.370	12.832	4.155	2.120	47.54	6.31	28.77	−0.12	+0.12	−0.06
carboxylic acid	7.030	12.310	3.985	2.020	48.78	6.31	28.59	+0.12	+0.12	−0.24
$C_{11}H_{17}O_3Br$. C − 47.66; H − 6.19; Br − 28.83	4.910	8.570	2.780	1.435	47.63	6.31	29.23	−0.03	+0.12	+0.40
γ-Bromopropylcyclopentanone semicarbazide *	6.390	9.650	3.565	1.950	41.21	6.24	30.52	−0.02	+0.09	+0.03
$C_9H_{16}NO_3Br$. C − 41.23; H − 6.15; Br − 30.49	6.650	9.930	3.680	2.000	41.31	6.28	30.49	+0.08	+0.03	0
3-(n-bromophenyl)-1,1-dichloropropene-1	7.336	10.913	1.790	4.164	40.59	2.73	56.76	−0.05	−0.08	+0.05
$BrC_6H_4CH_2CH = CCl_2$. C − 40.64; H − 2.65; Cl + Br − 56.71	11.475	17.075	2.779	6.512	40.61	2.71	56.77	−0.03	−0.06	+0.06
β-Chlorophenyliodonium chloride	5.700	6.700	1.295	3.772	32.08	2.52	66.18	+0.16	+0.28	+0.60
$C_8H_7Cl_2I$. C − 31.92; H − 2.34; Cl + I − 65.58	6.018	7.000	1.320	3.930	31.74	2.45	65.31	−0.18	+0.11	−0.27
1,2,3,3-Tetrachloropropene-1	8.925	6.449	0.900	7.080	19.77	1.13	78.77	−0.26	+0.01	−0.07
$C_3H_2Cl_4$. C − 20.03; H − 1.12; Cl − 78.84	9.603	6.988	1.263	7.593	19.86	1.47	79.07	−0.17	+0.35	+0.23
1,2,3,3-Pentachloropropene-1	8.692	5.347	0.475	7.169	16.79	0.61	82.48	0	+0.14	−0.15
C_3HCl_5. C − 16.79; H − 0.47; Cl − 82.63										
1,1,1,2,2,3-Hexachloropropane	6.600	3.455	0.645	5.595	14.29	0.92	84.77	−0.08	+0.12	−0.06
$C_3H_2Cl_6$. C − 14.37; H − 0.80; Cl − 84.83	8.510	4.392	0.707	7.204	14.09	0.93	84.65	−0.28	+0.13	−0.17

---

* The nitrogen oxides were trapped with a dry absorbent prepared according to Klimova and Korshun's method [10].

TABLE 5

Simultaneous Determination of Carbon, Hydrogen, Chlorine, and Iron

Test material	Weight of sample	CO_2	H_2O	Cl	Fe_2O_3	Found in %				Difference in %			
	In mg					C	H	Cl	Fe	C	H	Cl	Fe
2-Isobutylnaphthopyryl ferrochloride $C_{17}H_{17}OFeCl_4$ C–46.94; H–3.94; Cl–32.61; Fe–12.81	9,390	16,190	3,090	3,050	1,695	47,05	3,68	32,48	12,62	+0,11	−0,26	−0,13	−0,19
	5,540	9,532	1,870	1,825	1,005	46,96	3,74	32,65	12,57	+0,02	−0,20	−0,04	−0,24
2-n-Amylnaphthopyryl ferrochloride $C_{18}H_{19}OFeCl_4$ C–48.14; H–4.27; Cl–31.59; Fe–12.44	5,345	9,430	2,110	1,690	0,935	48,14	4,42	31,62	12,22	0	+0,15	+0,03	−0,22
	6,050	10,930	2,365	1,915	1,065	48,21	4,37	31,65	12,31	+0,07	+0,10	+0,06	−0,13

in the decomposition products.* It is known that such materials or dichloroethane, ethyl chloride and iodide, dichloro- and trichloroethane, and also the halogen hydrides, etc., are oxidation inhibitors at insignificant concentrations. The extent to which carbon is oxidized to carbon monoxide may therefore depend on the concentrations of these materials. It may be concluded therefrom, that the fact that carbon monoxide has actually been found to be present by us in the gaseous combustion products of various organic halogen products is not unexpected. It is clear that in these cases inhibition of the oxidation process occurs, this being precisely characteristic of the combustion of halogen-containing materials. No such phenomenon was observed during pyrolytic combustion of a large number of other organic compounds which did not contain halogens.

We believe the fact that, on isolating the halogen immediately after decomposition of the material, all the carbon is quantitatively converted into CO_2 in the oxidizing zone, does not contradict the viewpoint advanced above (Fig. 2). All the same, when this technique for determining halogen is used, the possibility of simultaneous determination of hydrogen with the carbon is excluded. Accordingly, we think that it is better to work in the presence of a platinum contact, which ensures complete oxidation of carbon to CO_2 during pyrolytic combustion of halo-organic compounds without having to modify any of the conditions used for the rapid method [9]. It then becomes possible to carry out simultaneous determination of halogen, carbon, and hydrogen.

It should be noted that during combustion of bromoanthracene, bromo-naphthalene, and hexachlorocyclohexane by the usual method, but at a temperature of the oxidizing zone of 1100°, good results were obtained for carbon (Table 2). All the same, such a method cannot be recommended since the quartz tubes frequently go out of order.

There is no need to use platinum catalysts when only halogen is to be determined.

Table 3 contains results for the determination of halogens by the normal method. Simultaneous determination of carbon, hydrogen, and halogens, apart from the use of platinum contacts and heating the silver to 550-600°, does not differ otherwise from the method used for simultaneous micro-determination of C, H, and S [9].

---

* A qualitative test for phosgene in the gaseous pyrolysis products gave negative results.

It should be noted that during determination of carbon, hydrogen, and halogens by the given method, results for carbon and hydrogen can be obtained with the usual accuracy, while for halogens – sometimes – the accuracy is lower, probably because of errors in weighing. In such cases it is recommended that greater sample weights be taken (~ 7-8 mg). It is possible to determine four elements, carbon, hydrogen, halogen, and metal, in compounds containing a metal.

Table 4, contains results for simultaneous determination of carbon, hydrogen, and halogens (chlorine, bromine, and iodine); while Table 5 contains results for determinations of carbon, hydrogen, chlorine, and iron on one aliquot (4-11 mg).

The accuracy for determinations of carbon and hydrogen varies from ± 0.1 to 0.3%, while that for halogen varies from ± 0.1 to 0.6% absolute.

SUMMARY

It has been established that during pyrolytic combustion of halogen-containing materials in an empty tube, carbon monoxide is formed; this leads to low results for carbon.

For simultaneous determination of carbon, hydrogen, and halogens, it is best to carry out pyrolytic combustion in the presence of a platinum catalyst. When only halogen is to be determined there is no need to use platinum contacts.

LITERATURE CITED

[1] M. O. Korshun and N. S. Sheveleva, Proc. Acad. Sci. 60, 63 (1948).

[2] M. O. Korshun and N. E. Gelman, "New Methods of Elemental Micro-Analysis", State Chem. Press, Moscow, 1949, p. 54.

[3] R. Belcher and C. Spooner, J. Chem. Soc. 313 (1943).

[4] G. Ingram, Analyst, 73, 548 (1948).

[5] A. F. Colson, Analyst, 73, 541 (1948).

[6] G. L. Stragand and H. W. Saffard, Anal. Chem. 21, 625 (1949).

[7] R. Teston and F. E. McKenna, Anal. Chem. 19, 193 (1947).

[8] A. Lacourt and Ch. T. Chang, Bull. soc. chim. Belg. 50, 68, 115, 135 (1941); 52, 157, 175 (1943).

[9] M. O. Korshun, J. Anal. Chem. 7, 96, 101 (1952) (T. p. 111, 117)*; M. O. Korshun and N. S. Sheveleva, ibid. p. 104 (T. p. 121).*

[10] V. A. Klimova and M. O. Korshun, J. Anal. Chem. 6, 230 (1951).

Received March 30, 1955

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

AN EXPRESS DROP-DESORPTION METHOD FOR THE SEPARATION AND IDENTIFICATION OF SHORT-LIVED RADIOELEMENTS

K. V. Troitsky

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow

At present the methods which are used for separation and identification of radioactive elements take a long time; they are based on the addition of a non-radioactive element – the "carrier" – to the separated solution, the radioactive isotope of this element being the one which it is required to determine; this element is then isolated by means of a suitable specific reagent. Ordinary laboratory technique (filtration, washing of precipitates, etc.), takes a lot of time; such methods therefore are not applicable to the isolation and identification of short lived radioelements with half-life periods of less than one hour.

In order to cut down the time required for carrying out an analysis, we should like to put forward a drop-desorption method for isolating and identifying short lived radioelements; this technique consists in placing a solution containing a mixture of different radioelements on a filter paper; a small amount of a soluble salt of the element whose radioactive isotope is to be determined is then placed on the filter paper as a carrier. After the paper has soaked up the solution, it is treated with an appropriate specific reagent, which forms in the paper pores an exceptionally finely dispersed precipitate (100-200 γ). To remove other (foreign) radioelements from the filter paper pores, the paper, after drying over a hot plate, is dipped in acid solution (hydrochloric, nitric, etc.); on doing this, desorption of the other radioelements takes place from the surface of the paper, and only the precipitate of "carrier" containing the radioelement to be determined is held back on the paper surface. The precipitate of carrier should not be appreciably soluble in the acid used. Other reagents (alkalis, ammonia, solutions of various salts, etc.) can sometimes be used for desorption of other radioelements from the paper surface.

Here is an example of the technique. When a mixture of various radioelements contains radioactive copper, the latter can be separated out on filter paper with rubeanic acid which gives a black precipitate. On a 30 mm diameter filter paper is placed the test radioactive solution, containing a copper salt as carrier (150-200 γ Cu). After evaporation of excess solution until the paper is damp, a few drops of an alcoholic solution of rubeanic acid is placed on it. A finely dispersed precipitate of copper rubeanate is formed in the paper pores. The paper is then dipped in a dilute hydrochloric acid solution (1:10) for 5 minutes; when this is done, only radioactive copper stays on the surface of the paper together with the carrier (as long as the solution does not contain Ni, Co, Hg, Pt, Ag, and Ru) while the other radioelements are desorbed from the paper surface and go into solution. After the paper has been dried the yield of radioactive copper can be measured with an ionization counter, and the half-life period determined.

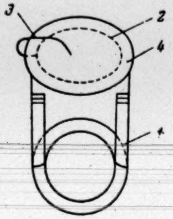
Radioactive niobium and zirconium can be separated by means of phenylarsonic acid.

For the isolation of short lived radioelements various types of spot precipitation reactions on filter paper can be used; it is essential however, that the reagent chosen should be specific for the radioelement to be isolated. Moreover, the precipitate formed on the filter paper should be sparingly soluble in dilute acid.

The method suggested may find wide application for isolating various radioelements, since it is based on numerous spot precipitation reactions leading to the formation of both colored and colorless precipitates [1-3]; it can also be used for the rapid isolation of various long-lived radioelements.

EXPERIMENTAL TECHNIQUE

During measurement of radioactive materials whose radiation is of low energy, the uniform distribution of the material on the target surface is of essential importance, otherwise when the distribution is not uniform part of the radiation is absorbed in the layer.



In order to get uniform distribution of the radioactive precipitate in a thin layer we used circles of ashless filter paper (blue ribbon quality) 30 mm in diameter. A miniature set-up (see diagram) was used in order to place the various solutions on this target; this held the filter paper while the solution was being applied from a graduated buret, and also during evaporation of the solutions.

This set-up consists of a ring 1 made from copper wire 1-2 mm diameter, which serves as a base,; the top part consists of ring 2 made from a fine platinum wire 0.1-0.2 mm in diameter.

Solutions were placed on the paper target as follows: the circle of filter paper 4 is placed in the set-up and fixed in position with a spring made of platinum wire 3. 0.1-0.2 ml of test solution is then measured out from a buret onto the center of the paper disc, and the set-up plus target placed on a hot plate covered with asbestos; the solution thereupon evaporates rapidly. After drying, the target is removed from the set-up, fastened to a leaf of writing paper and the activity measured on a Type B apparatus with a torsion counter.

Numerous measurements of samples with low and high radiation energies (0.2-3.5 Mev.) showed that deviations between identical samples vary within the limits ± 1- 5% of the mean. When the drop-desorption method is used, after the test solution has been placed on the target, evaporation is continued until the paper is in a damp state; the appropriate reagent, which forms a precipitate with the test element on the paper surface, is then added. The target is finally dried over the hot plate and the other radioelements removed from the paper surface by immersion in a solution of the appropriate acid or other desorbent.

EXPERIMENTAL RESULTS

The drop-desorption method of isolating and identifying radioactive elements has been developed by us in the course of several years (up to the present more than 1000 tests have been carried out).

Preliminary tests showed that precipitation of radioactive elements as sulfides leads to appreciable coprecipitation of other radioelements;; accordingly it is not expedient to isolate radioelements as the sulfides.

Table 1 contains results on the determination of the purity of radioactive indicators; they indicate that the method is satisfactory. It should be noted that it is necessary, in each individual case, to correct for the solubility of the precipitates in acid, and also to find the optimum amount of "carrier".

We also studied the effect of various elements on the co-precipitation of radioactive Zn^{65}. In all tests, 50 γ of Zn was taken as a carrier in each one. It follows from Table 2 that Zn^{65} is hardly co-precipitated at all during precipitation of the ions of copper, cobalt, iron, and zirconium by a number of organic reagents (rubeanic acid, cupferron, phenylarsonic acid, etc).

In comparison with precipitates formed in aqueous solution, the precipitates which are deposited on filter paper, have finer particles; thus, magnification of 700-900 was insufficient to distinguish between individual particles.

The results given in Table 3 are those obtained during a study of the effect of certain reagents on a complex mixture of radioactive elements, in solution without a carrier. It follows from Table 3 that in most cases, parallel tests give coincident results, indicating that precipitation of certain radioelements by the reagents occurs. Of course, most of them are group reagents, but, under certain conditions, they can be used for isolating individual radioelements. The following elements form precipitates with $K_4Fe(CN)_6$: Hg, Bi, Cd, Sn, the rare earths, Zr, Th, Tl, Zn, Mn, Ni, Sb, Nb, V, Co, Fe, U, Cu and Mo; accordingly, Sb, Ce, Zr, Nb, Eu, and Y can

TABLE 1

Test number	Amount of carrier on the filter	Radioactive element determined	Precipitating reagent	Activity yield on the filter	Observations
1	20,5 γFe	Fe^{59}	$K_4Fe(CN)_6$	89,7	Unpurified indicator iron
2	65 γFe	Fe^{59}	$K_4Fe(CN)_6$	96,0	After purification of the indicator iron by extraction with ether
3	57 γCo	Co^{60}	Rubeanic acid	98,2	
4	520 γW	W^{185}	Hydrochloric acid solution of $SnCl_2$	94,5	Precipitate in the form of the blue oxide W_2O_5

TABLE 2

Test number	Amount of carrier	Radioactive element	Precipitating reagent	Activity yield on filter after desorption in %	Observations
1	152 γFe	Zn^{65}	$K_4Fe(CN)_6$	90,0; 92,7	A white precipitate is formed with zinc $Zn_3K_2[Fe(CN)_6]_2$
2	150 γCu	Zn^{65}	$K_4Fe(CN)_6$	71,8; 86,2	Formation of the precipitate $Cu_2[Fe(CN)_6]$ or $CuK_2[Fe(CN)_6]$
3	150 γCu	Zn^{65}	Rubeanic acid	0,0; 0,0	
4	152 γCo	Zn^{65}	ditto	0,0; 0,1	
5	152 γFe	Zn^{65}	Cupferron	0,0; 0,0	Precipitation carried out from a weakly acid medium
6	138 γZr	Zn^{65}	ditto	1,4; 1,0	ditto
7	152 γCo	Zn^{65}	α-Nitroso-β-naphthol	0,0; 0,0	» »
8	138 γZr	Zn^{65}	Phenylarsonic acid	0,0; 0,0	» »
9	150 γBa	Zn^{65}	Na_2SO_4	0,0; 0,0	» »

be separated from Solution IV by this reagent. This reagent separates practically equal amounts of the radioelements during precipitation with iron and copper ions. Radioactive Ru^{103} and Ru^{106} are separated as the rubeanates. Zr and Nb are precipitated with phenylarsonic acid, while elements of the rare earth group are precipitated as the fluorides.

TABLE 3

Experiments Using Solution IV *

Test number	Amount of carrier	Precipitating reagent	Activity yield on the filter after desorption in %	Observations
1	32 γRu	Rubeanic acid	6,1; 5,7	
2	50 γCu	ditto	3,2; 4,1	
3	78 γNi	» »	4,3; 3,9	
4	60 γCo	» »	9,6; 9,1	
5	147 γFe	$K_4Fe(CN)_6$	11,9; 11,7	
6	150 γCu	$K_4Fe(CN)_6$	13,3; 12,2	
7	108 γZr	Phenylarsonic acid	5,3; 6,8	
8	200 γCe^{IV}	» »	19,3; 21,2	
9	120 γAg	HCl	0,4; 0,3	
10	120 γCs	Silicomolybdic acid	8,7; 10,9	The radiation energy of the sample corresponds to that of Cs^{137}
11	120 γBa	K_2SO_4	41,9; 48,7	
12	360 γCe^{III}	HF	24,7; 23,5	
13	100 γCu	Na_2S	19,5; 18,2	
14	90,4 γRu	Na_2S	11,0; 12,9	

---

* A mixture of the following radioactive elements are contained in Solution IV: strontium, zirconium, niobium, ruthenium, cerium, yttrium, and some others.

We believe that this method could be applied as an express method even for the analysis of this complex mixture of radioelements; in such a case, group reagents such as $K_4Fe(CN)_6$, K_2SO_4, HF and others, can also be used for separation of a mixture of radioelements.

In order to determine radioactive Ru as the rubeanate, we developed a special express method, which gives good results. Table 4 contains the results for the determination of radioactive Ru in two different solutions. These tests showed that on precipitation of radioactive Ru on the filter as the sulfide, other radioelements are trapped at the same time, while when Ru is precipitated as the rubeanate, it separates out as the pure radioactive isotopes Ru^{103} and Ru^{106} [4].

The method we are suggesting has also been used for the isolation and identification of short-lived radioelements during activation analysis. Beryllium oxide, metallic aluminum foil, and very pure metallic copper were irradiated with neutrons. By this technique radioactive Mn^{56}, Sr^{87}, Na^{24}, and some rare earth elements were detected in beryllium oxide.

The following radioisotopes: Cu^{64}, Ga^{72}, Na^{24} and Eu^{152} [4], were detected in the metallic aluminum foil.

Some radioactive isotopes of rare earth elements were detected in the copper metal in addition to large amounts of Cu^{64}.

As is evident from what has been said above, the drop-desorption method of isolating and identifying radioactive elements can find wide application. The isolation and identification of radio elements on colorless precipitates ($BaSO_4$, AgCl, etc.), is possible.

The method suggested permits speeding of work on isolation and identification of radioelements by a factor of ten as compared with ordinary methods, and ensures in many cases quantitative determination of the content of short-lived radioelements in a mixture of radicelements for which no other rapid methods of analysis are available. One can instance, for example, determination of Ru in certain solutions. Usually it is determined by distillation of RuO_4 from alkali solutions. To carry out this determination, it takes one analyst 1-2 days; according to the method which we have suggested, Ru can be isolated and determined in 10-20 minutes using a minimum amount of carrier (50-200 γ) as Ru rubeanate.

TABLE 4

Test number	Solution number	Precipitate of collector	Amount of carrier	Activity of sample after desorption %	Separation of radio isotopes
1	IV	Cupric sulfide	100 γ Cu	19,5; 18,2	Radioactive Ru mixed with other radioelements
2	VIII	» »	127 γ Cu	4,1; 4,9	ditto
3	IV	Ru sulfide	90,4 γ Ru	11,0; 12,9	» »
4	VIII	» »	118 γ Ru	6,6; 5,8	» »
5	IV	Copper rubeanate	100 γ Cu	2,2; 2,1	Ru^{106}
6	VIII	» »	127 γ Cu	0,7; 0,5	Ru^{103}, Ru^{106}
7	IV	Ru rubeanate	113 γ Ru	4,9; 4,3	Ru^{106}
8	VIII	» »	118 γ Ru	1,6; 1,0	Ru^{103}, Ru^{106}
9	IV	Extraction of Ru with ether after reaction with diethyldithiophosphoric acid [5]	68,5 γ/ml Ru	4,3; 4,8	Ru^{107}
10	VIII	»	68,5 γ/mlRu	1,3; 1,3	Ru^{103}, Ru^{106}

If the test solution contains certain mixtures of radioactive elements, then, using the reference book [6], it is possible to select a specific organic precipitant for precipitating the radioelement with a carrier.

SUMMARY

1. The drop-desorption method of isolating and identifying radioactive elements has the following advantages:

a) formation of precipitates on filter paper and desorption of other radioelements takes a very short time (10-15 minutes);

b) only a small amount of "carrier" (150-200 γ) is required for analysis of the radioelements;

c) the use of organic reagents ensures that the precipitates obtained are free from contamination by other radioelements;

d) formation on the surface of filter paper fibrils of a fine and uniform layer of precipitate favors more accurate measurement of the activity by an ionization counter;

e) the method improves the chemist's output 5-10 times.

2. The express drop-desorption method of isolating and identifying radioactive elements may find application in:

a) the analysis of various radioactive solutions in factory laboratories, scientific-research institutes and in actual production. This method is particularly effective for the analysis of short-lived radioactive elements (with half-life periods of less than 1 hour);

b) in the activation method of analysis;

c) for determination of impurities in various radioactive indicators, etc.

The method suggested for determination of radioelements is based on the use of numerous precipitation spot reactions, leading to the formation of both colored and colorless precipitates.

LITERATURE CITED

[1] N. A. Tananaev, "Spot Analysis", State Chem. Press, 1954.

[2] F. Feigl, "Spot Analysis", State Chem. Press, 1937.

[3] L. M. Kulberg, G. S. Altman and R. P. Veltman, "Spot Analysis", State Chem. Press, 1951.

[4] I. P. Selinov, "Atomic Nuclei and Atomic Transformations", Vol. 1, State Theor. Lit. Press, 1951.

[5] A. I. Busev, J. Anal. Chem. 4, 49 (1949).

[6] Reference Book "Chemical Reagents and Preparations", Edited by V. I. Kuznetsov, State Chem. Press, 1953, pp. 583-631.

Received March 29, 1956

SEPARATION OF BERYLLIUM FROM ALUMINUM AND OTHER ELEMENTS BY AN EXTRACTION METHOD

I. P. Alimarin and I. M. Gibalo

The M. V. Lomonosov Moscow State University

Most methods for determination of beryllium are based on preliminary separation of this element from a number of other elements, in particular, from aluminum and iron. The chemical properties of beryllium and aluminum are very similar, and their quantitative separation presents considerable difficulties. Many of the methods in use at present are based on precipitation reactions; they are not sufficiently accurate and fast.

We set ourselves the problem of developing a new extraction method for separating beryllium and aluminum using two complexing compounds, acetylacetone and Trilon B (Complexone III). Acetylacetone [1], and Trilon B [2], form stable inner complexes with many elements. Beryllium acetylacetonate is a fairly stable compound (pK 12.36) [3]; beryllium complexonate is appreciably less stable [1]. Aluminum, on the other hand, forms a more stable complex with Trilon B (pK 16.13) [4] than with acetylacetone. The acetylacetonates of many elements are soluble in organic solvents [5, 6], while the complexonates are not soluble.

We studied the behavior of the acetylacetonates of a number of Group II, III, and IV cations, during extraction with various organic solvents (carbon tetrachloride, chloroform, n-butanol, isoamyl alcohol) in the presence of Trilon B.

Tests showed that only beryllium acetylacetonate is readily extracted in the presence of Trilon B. Carbon tetrachloride was found to be the best extractant. The acetylacetonates of the other divalent cations were not extracted by any of the solvents tried. As regards the trivalent cations (Al, Fe), they were only extracted in a strongly ammoniacal medium (pH 12). No extraction was observed in weakly acid or weakly alkaline media. Such behavior on the part of the trivalent cations can, probably, be explained by the fact that they form with Trilon B [7], in contrast to the divalent cations, two types of ions $[\mathrm{Me^{III}R}]^-$ and $[\mathrm{Me^{III}R(OH)}]^{2-}$ (R is the radical of ethylenediaminetetracetic acid). Ammoniacal media favor formation of ions of the type $[\mathrm{Me^{III}R(OH)}]^{2-}$.

Hydroxyl ions which coordinate around the central atom, lower the stability of a complex compound. This probably explains the sharp decrease in stability of aluminum complexonate in ammoniacal media. If acetylacetone* is present in the complexonate solution, it is not the complexonate that is formed, but the more stable aluminum acetylacetonate. The reaction can be represented by the following equation:

$$\begin{array}{ccc} \mathrm{Al(Ac)_3} + \mathrm{R}^{4-} & \rightleftharpoons & [\mathrm{AlR}]^- + 3\,\mathrm{Ac}^- \\ \text{ammoniacal} & & \text{weakly acid or weakly} \\ \text{medium} & & \text{alkaline medium} \end{array}$$

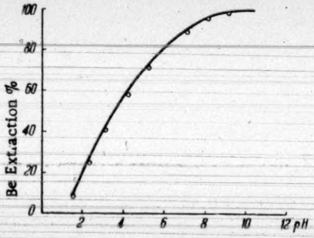
---

* Ac - acetylacetone

The capacity of acetylacetonates to be extracted by organic solvents coupled with the considerable difference in the stability of the acetylacetonates and complexonates of aluminum and beryllium, were used by us for separating beryllium from aluminum and other elements.

Extraction of Beryllium

The acetylacetone used in our work was given a preliminary purification. In order to remove acetic acid, 200 ml of acetylacetone was shaken with 20 ml of dilute 1: 10 ammonia solution, and then twice with 20 ml of distilled water. The acetylacetone purified in this way was redistilled, and the fraction boiling at 135-137° collected.



Conditions for extraction of beryllium acetylacetonate with carbon tetrachloride in the presence of Trilon B were studied in relation to a number of factors (pH of the medium, concentrations of Trilon B and acetylacetone, respectively, presence of other ions, etc.).

Experiments were carried out with 10 mg of beryllium in a volume of 10 ml, in the presence of 5 ml 0.05 M Trilon B solution and 5 ml of 15% aqueous acetylacetone solution. Extraction was repeated three times, 7 ml of carbon tetrachloride being used each time. It was established that the concentration of Trilon B, and the presence of other ions (SO_4, Cl, NO_3, and NH_4) have hardly any effect on beryllium extraction. The percentage extraction of beryllium depends to a considerable extent on hydrogen ion concentration (diagram). Beryllium is practically completely extracted at a pH of 9.

Experiments carried out under similar conditions with solutions of the salts of iron (III), aluminum, chromium, cobalt, nickel, manganese, zinc, cadmium, lead, copper, calcium, and magnesium, showed that these cations are not extracted, and can be separated from beryllium.

Separation of Beryllium from Aluminum

On the basis of the differences in properties of the acetylacetonates and complexonates of beryllium and aluminum, we developed an extraction method for separating them which is described below.

To a solution containing beryllium and aluminum, in a separating funnel (10-15 ml, pH 4-5), are added successively 12-15 ml of 0.05 M aqueous Trilon B solution, 5 ml of a 15% aqueous acetylacetone solution and 2 drops of concentrated ammonia; this mixture is thoroughly mixed and then 8 ml of carbon tetrachloride added, and the whole shaken for 5-7 minutes. After shaking, the layer of organic solvent is poured off and the extraction repeated twice again; each time 5 ml of acetylacetone is added as well as 2 drops of concentrated ammonia, and 8 ml of carbon tetrachloride.

Having collected the three aliquots of carbon tetrachloride in a separating funnel, 20 ml of water and 15 ml of concentrated hydrochloric acid are added, and the beryllium re-extracted into the aqueous layer. After removal of the organic phase, the aqueous layer is evaporated almost to dryness; to the dry residue is added 15-20 ml of water and 1 ml of concentrated hydrochloric acid, and beryllium precipitated with ammonia.

To the solution remaining, after removal of beryllium, is added 4-5 ml of concentrated ammonia, 5 ml of acetylacetone, and 7 ml of carbon tetrachloride, and the aluminum extracted. Extraction is repeated three times. Aluminum is re-extracted from the organic phase in exactly the same way as beryllium, and is finally determined as Al_2O_3. Results are given in Table 1.

It follows from Table 1 that beryllium can be completely separated from aluminum. Experimental error does not exceed 0.4%. Aluminum could not be detected in the precipitate of beryllium oxide by qualitative tests.

TABLE 1

Determination of Beryllium and Aluminum After Separation by Extraction

Amount taken in mg		Amount found in mg	
BeO	Al_2O_3	BeO	Al_2O_3
19,32	—	19,30	—
—	18,94	—	18,91
3,86	23,67	3,85	23,62
11,58	18,94	11,60	18,94
19,32	18,94	19,29	18,93
23,16	1,89	23,11	1,90

TABLE 2

Results for the Determination of Beryllium in Beryllium Bronze (SO-110)

Sample taken in mg	Rated content of Be in mg	Be found in mg	Deviation in mg
209,1	4,30	4,28	—0,02
298,4	6,32	6,34	+0,02
153,2	3,24	3,21	—0,03

We used the method described above for the analysis of beryllium bronzes.

Determination of Beryllium in Bronze

We had at our disposal a standard sample of bronze (SO – 110), containing 2.12% Be, 0.176% Fe, 0.04% Al, 97.26% Cu and small amounts of other elements.

An aliquot of bronze 150 – 300 mg is dissolved in 10-15 ml of nitric acid (1 : 3) on heating. The solution is evaporated almost to dryness, the dry residue dissolved in 20-40 ml of distilled water, and transferred to a separating funnel; 6% aqueous Trilon B solution is then added, on the basis of 2 g Trilon B for each 100 mg alloy (volume of test solution 90-120 ml); this is followed by ammonia (1 : 1) until there is a faint smell of the latter, and the whole thoroughly mixed. 3 ml of acetylacetone and 12 ml of carbon tetrachloride are next added, and the whole shaken for 5-7 minutes. The organic solvent is poured off, and the extraction repeated twice again, each time 3 ml of acetylacetone and 12 ml of carbon tetrachloride being added. Beryllium is finally determined as BeO after re-extraction from the organic phase. After removal of beryllium, 5 ml of concentrated ammonia, 1 ml of acetylacetone, and 12 ml of carbon tetrachloride are added to the test solution, and the aluminum and iron extracted.

Results for determination of beryllium in bronze are given in Table 2.

This method can therefore be used for a fairly rapid and accurate determination of beryllium in bronze.

SUMMARY

1. The extractability of the acetylacetonates of aluminum, chromium, cobalt, iron, nickel, manganese, zinc, cadmium, lead, copper, calcium and magnesium by organic solvents (carbon tetrachloride, chloroform, n-butanol, and isoamyl alcohol) in the presence of Trilon B, has been studied.

2. Conditions have been found for the quantitative extraction of beryllium acetylacetonate in the presence of Trilon B, and for its separation from aluminum.

3. A comparatively rapid and accurate method has been developed for the isolation and determination of beryllium in bronze.

LITERATURE CITED

[1] J. F. Steinbach and H. Freiser, Anal. Chem. 25, 6, 881 (1953); 26, 2, 375 (1954).

[2] R. Pribil, Komplexony v Chemicke Analyse, Prague, 1953.

[3] L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, J. Am. Chem. Soc. 75, 11, 2736 (1953).

[4] G. Schwarzenbach, R. Gut and G. Ackerman, Helv. Chim. Acta 37, 937 (1954).

[5] J. A. Adam, E. Booth and J. D. Strickland, Anal. chim. Acta 6, 462 (1952).

[6] E. Abrahamczik, Mikrochim. Acta 36-37, 104 (1951).

[7] G. Schwarzenbach and W. Biederman, Helv. Chim. Acta 31, 459 (1948).

Received November 26, 1955

NEW REAGENTS FOR THE COLORIMETRIC DETERMINATION OF BERYLLIUM – BERILLON I AND II

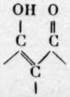
A. M. Lukin and G. B. Zavarikhina

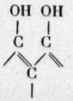
All-Union Scientific Research Institute for Chemical Reagents, Moscow

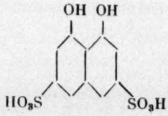
The most important reagents for the detection and determination of beryllium by gravimetric, colorimetric and fluorescence methods are the following: 1) acetylacetone [1]; 2) tannin [2, 3]; 3) aluminon [4, 5]; 4) quinalizarin [6-8]; 5) curcumin [6]; 6) alizarin-3-sulfonic acid [9]; 7) the azo dye from orsine and diazoparanitroaniline [10-12]; 8) naphthazarine [13-16]; 9) alkanine [13-16]; 10) morine [17]; 11) 1-amino-4-hydroxyanthraquinone [18]; 12) quinizarin [19]; 13) naphthachrome green G [20]; 14) quinizarin-2-sulfonic acid [21]; 15) sulfosalicylic acid [22, 23]; 16) 1,4,5,8-tetrahydroxyanthraquinone [24]; 17) acid alizarin blue BB (1,2,4,5,6,8-hexahydroxyanthraquinone-3,7-disulfonic acid) [25]; 18) thoron [26]; 19) 2-(o-hydroxyphenyl)-benzthiazole [27]; 20) solochrome bright blue B [28]. The most valuable reagent found hitherto for colorimetric determination of beryllium was thought to be quinalizarin [29]; this reagent however has certain essential disadvantages (See e.g. [8]).

The absence of really good reagents for the colorimetric determination of beryllium and the increased interest displayed in this metal, particularly in recent years, was the reason why we undertook this work.

In looking for new reagents for beryllium we started off on the basis of the following considerations. It can be readily seen that the molecules of the overwhelming majority of the reagents listed above, despite the considerable variety in their structure, possess a characteristic group of atoms (I), which is met either in the form of a o-hydroxycarboxylic acid (Reagents 3, 13, 14, and 20) or in the form of 1, 3-hydroxyoxogroups (Reagents 1, 4, 5, 6, 8, 9, 10, 11, 12, 14, 16 and 17). The latter is found in the molecules or in the form of a link in the aliphatic chain of the reagent (acetylacetone, curcumin – see a similar treatment in [30]) or as a part of the skeleton of various hydroxy-substituted flavones, anthraquinones, and naphthaquinones (the group peri-hydroxy-oxo) (it is precisely to this type that the largest number of the reagents listed above belong).


(I)


(II)


(III)

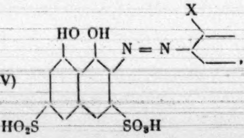
In order to find a new and more effective reagent for beryllium one could continue to study the already widely used anthraquinone compounds. This is what Mustafin and Kulberg [24], and Barskaya and Shemyakin [25], did recently. We decided otherwise.

Group (II) is known to be chemically similar to Group (I), and they are very readily converted into one another. On this basis we decided to use as starting material readily available chromotropic acid (III), which contains Group (II). Among the azo dyes which can be derived from chromotropic acid as a basis, we hoped to find a compound which would be a valuable reagent for beryllium.

We should like to point out that chromotropic acid itself, or as a component of several azo dyes has already been suggested by others before us more than once, as a reagent for a number of cations (see, e.g. [31-43]). There are also indications that some of the products formed between chromotropic acid, e.g. with diazo compounds from o- and n-aminophenols [31], and from anthranilic acid [37], can react with beryllium (as well as with many other cations). Nevertheless, we could not find any statements to the effect that such compounds are of practical value as reagents for the cation we are interested in. The indications mentioned above only confirm, and that indirectly, the correctness of our approach. From all the published material it also follows that the series of compounds we had marked out for study could hardly lead to the discovery of a sufficiently selective reagent. Accordingly, if one could get hold of a representative of this class which would satisfy all the other requirements which a reagent for beryllium has to meet, its practical use would only be possible by using suitably chosen masking agents.

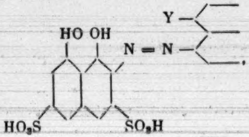
Of the considerable number of mono-azo dyes, already known, or theoretically possible, which are based on chromotropic acid, we decided to concentrate on two series: with Group (IV) and with Group (V).

(IV)



, where X = H, COOH, SO$_3$H, AsO$_3$H$_2$, OH or NO$_2$

(V)



, where Y = H, OH or O =

The observations made above provided an indirect basis for the necessity of studying Series (IV). With respect to Series (V), we decided to study this on the basis of certain analogies which exist between ortho substituted compounds of the benzene series, and peri substituted compounds in the naphthalene and anthraquinone series.

In order to prepare azo dyes of Series (IV), chromotropic acid was combined with diazo compounds of the following amines: 1) aniline; 2) anthranilic acid; 3) orthanilic acid; 4) sulfanilic (for comparison with the former); 5) o-aminophenylarsonic acid; 6) o-aminophenol, and 7) o-nitroaniline; for dyes of Series (V), with diazo compounds from: 1) α-naphthylamine; 2) H-acid; 3) K-acid, and 4) α-aminoanthraquinone.

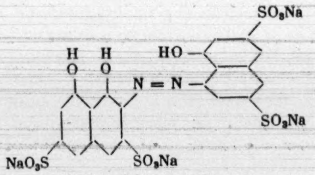
Since many of the compounds synthesized are already known in the literature, and the method of combining chromotropic acid with the respective compounds is well known and has been described in detail (see e.g. [44], p. 122; [45], p. 160; [46], p. 99 etc.), we shall not dwell on the details of the synthetic part of our work. We shall merely point out that all the 11 compounds listed, plus some additional ones which were synthesized, were isolated in a chemically pure state; this was confirmed by analysis.

A study of the 11 compounds as analytical reagents led to the following results.

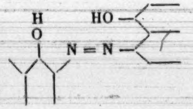
It was established, first of all, that all the test compounds actually react, though to varying extents, with beryllium. The hypothesis on which the present work is based was therefore completely confirmed. Nevertheless, it turned out that the contrast and sensitivity of the color reactions with the beryllium ion was very poor in most of the dyes; only the product formed between chromotropic acid and diazotized H-acid (VI) was worthy of special attention: this gives, in aqueous alkaline media (pH 12-13), a violet solution, which on reaction with beryllium ions changes to a stable pure blue; the sensitivity of this reaction is 0.2 γ Be in 5 ml, with good contrast in the limits 0.2-7 γ Be. It was also established, as was to be expected, that this compound does not in itself exhibit a high selectivity; thus, in the medium indicated, this reagent reacts with 10 cations. In order to enhance the selectivity we used Trilon B, which has already been successfully used for the gravimetric determination of Be [47]. In actual fact, addition of Trilon B enhanced the selectivity of the new reagent appreciably without altering its sensitivity. The product formed between chromotropic acid and diazotized H-acid was therefore considered worthy of further study in more detail as a potential reagent for beryllium. This detailed analytical investigation which was carried out by G. G. Karanovich, confirmed our preliminary conclusion on the advantages of this new reagent over quinalizarin [48 and 49].

Under the designation Berillon II IREA, this reagent has already been tested in a number of laboratories with positive results.

In order to accumulate experimental material to explain the chemistry of the interaction of the new reagent with beryllium, it was of interest to try and establish the significance and role of each functional group in the reagent molecule. In order to settle this question, we synthesized some more related azo compounds, and tested their color reactions with beryllium. Choice of these last azo compounds was determined by the following considerations.



(VI)



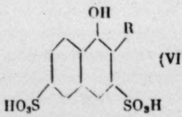
(VII)

Two ring-forming groups can be detected in azo dye (VI): the peri-dihydroxy (II) of the original chromotropic acid, and the orthohydroxy, peri-hydroxy[1] to the azo group (VII) of the dye. While we have already characterized above the role and significance of the first group, it was expedient to make compounds containing this second group, and, in particular, to find out whether it independently ensures color reactions between the compounds containing it and beryllium. With this aim in view we synthesized four compounds: (VIII), (IX), (X), and (XI), which only contain Group (VII); Group (II) being absent. In order to make more sure, in addition to (VIII), its isomer (XII) was also synthesized.

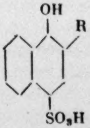
Investigation of the analytical properties of all these dyes just mentioned, led to the following results: 1) it appears that the four materials, i.e., (VIII) - (XI), fairly distinctly, but in most cases to a lesser degree than (VI), react with beryllium; consequently, Group (VII) is itself, apparently, just as characteristic for Be as the peri-dihyroxy of Group (II). The new group for Be (VII), has already been described in the literature, but there it was described as characteristic for boron [50]; 2) comparison of the properties of these same four azo dyes, showed that the most interesting compound is (X), i.e. the compound formed between the diazo compound prepared from H-acid, and H-acid itself; it gives similar contrasted color reactions with beryllium as Berillon II, but only in an acetate buffer (pH 5.6-6.0), not in an alkaline medium; moreover, it reacts with Co to give more contrasting colors than with Be. The sensitivity of this reagent, in both instances, is very good (equal to 0.2 γ of each cation in 5 ml) with good contrast. From these preliminary results, confirmed later by detailed study, also carried out by G. G. Karanovich [49], it developed that Compound (X), which we called Berillon I*, may be of decided interest in analytical practice, though to a lesser extent than Berillon II*. It is worthy of note that the product isomeric with (X), formed between K-acid and the diazo compound from H-acid, viz.(XI), does not possess sufficiently interesting analytical properties.

---

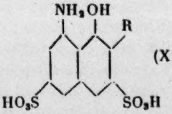
* The Roman ciphers following the reagents do not indicate the order in which they were discovered.



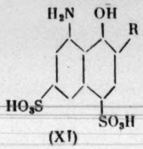
(VIII)



(IX)

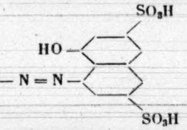


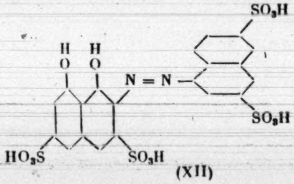
(X)



(XI)

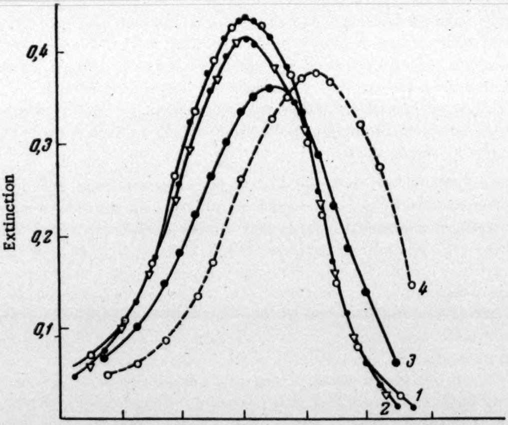
where R =





(XII)

Thus, the results obtained confirm that the properties of practical value in any reagent depend, apparently, in equal degree on three structural factors: 1) a characteristic group; 2) the skeleton of the molecule; and



Absorption curves for 0.001% aqueous solutions of Berillon: 1) pH 6-7; 2) pH 2-3; 3) pH 12-13; 4) pH 12-13 + Be.

3) the composition and location of additional substituents. In looking for new reagents, these factors must always be studied from all points of view; it is only by doing this that one can be assured of getting a reagent with optimum properties.

Comparison of the properties of Compounds (VIII) and (XII), which differ from Compound (VI) by the absence of only one hydroxyl group in varying positions, testifies to the fact that even on keeping all other conditions the same, the presence of only one group, (II) or (VII), does not ensure the existence of properties of value in practice. Only a combination of these groups, as in (VI), leads to a reagent of maximum interest.

Results of a study of the compound formed between Berillon II with beryllium will be the subject of a separate paper.

Since we did not find any published details on the synthesis of the azo compound corresponding to Berillon II, we have given a description of this compound as well as results characterizing its physicochemical properties.

EXPERIMENTAL

Synthesis * of Berillon II [8-hydroxynaphthalene-3,6-disulfonic acid-(1-azo-2')-1', 8'-dihydroxynaphthalene-3',6'-disulfonic acid as the di- or tetrasodium salt].

Preparation of the disodium salt. 3.8 g of chemically pure H-acid (the mono-sodium salt with two molecules of water of crystallization) are introduced into 50 ml of water containing 2 ml of concentrated hydrochloric acid. The suspension obtained is heated to 35°, and is diazotized at 30-35° in the course of 15 minutes with a solution of 0.7 g sodium nitrite in 5 ml water. The diazo compound formed as a suspension (straw-yellow needles) is kept for 10-15 minutes, and then cooled to room temperature; 4 g of chemically pure chromotropic acid (the disodium salt with two molecules of water of crystallization) and 5 g of sodium acetate in 60 ml of water are then added to the mixture.

As combination proceeds, the reaction mass becomes colored violet. Observations of the reaction mass under the microscope, shows that originally there is formed a mixture of straw-yellow coarse needles of the diazo compound with very fine brown crystals of the dye, the amount of which increases with time at the expense of a decrease in the diazo crystals; after 3 hours the latter disappear altogether. After mixing during the course of 5 hours from the time the components were combined, the reaction mass is filtered off; the paste obtained is dissolved by heating in 150 ml of water, and again filtered free from any turbidity which might be present; to the hot filtrate is added 50 ml of concentrated hydrochloric acid and the whole allowed to cool slowly. The precipitate which settles out on standing, in the form of homogeneous coarse violet-brown plates, is filtered off, washed with 25 ml dilute hydrochloric acid (1:3), after which it is subjected to further purification and finally dried (at 170° for analysis).

0.1942 g of material: 0.0390 g Na_2SO_4
0.2578 g of material: 0.3480 g $BaSO_4$
0.2858 g of material: 0.3812 g $BaSO_4$

Found %: Na 6.49; S 18.54; 18.33. Calculated %: Na 6.62; S 18.47. $C_{20}H_{12}O_{15}N_2S_4Na_2$.

The dye itself is a dark brown bronze powder; it forms raspberry colored solutions in water, alcohol, and 1% hydrochloric acid; in 1% sodium hydroxide and in 1% sodium carbonate the color is violet, while in concentrated sulfuric acid the color is blue; the material is practically insoluble in acetone, benzene, and carbon tetrachloride.

When the tetrasodium salt is to be prepared, the material isolated is not treated with hydrochloric acid. The procedure was similar to that described already with respect to the rest of the details.

0.1082 g of material: 0.0414 g Na_2SO_4
0.1020 g of material: 0.1288 g $BaSO_4$
0.1284 g of material: 0.1616 g $BaSO_4$

---

* N. S. Simonova helped in this part.

Found %: Na 12.39; S 17.35, 17.29. Calculated %: Na 12.46; S 17.37. $C_{20}H_{10}O_{15}N_2S_4Na_4$.

The properties of the tetrasodium salt are identical with those of the disodium salt, with the exception of lower solubility in organic solvents, in particular, in ethyl alcohol.

Curves are given above for the absorption spectra * of solutions of the reagent at three pH values, and of a solution of the product of its interaction with beryllium.

SUMMARY

1. Analysis of published results led to the conclusion that the following groups may be regarded as characteristic groups for beryllium: peri-hydroxyoxo (I) and peri- or 1,3 dihydroxy (II). During a search for new organic reagents for the colorimetric determination of beryllium, we prepared a number of azo dyes from chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid), which can be regarded as a carrier of one of the groups given above.

2. A study of the analytical properties of 12 azo dyes which were synthesized and isolated in a chemically pure form, and for which chromotropic acid was used as a starting material, led to the discovery of a new and valuable compound which is of practical value as a highly sensitive reagent for the colorimetric determination of beryllium; this new compound which is formed from chromotropic acid and the diazo compound prepared from H-acid is called Berillon II (VI) [8-hydroxynaphthalene-3,6-disulfonic acid-(1-azo-2')-1',8'-dihydroxynaphthalene-3',6',-disulfonic acid (as the di- or tetrasodium salt)].

3. The reagent is particularly suitable for beryllium determination at a pH of 12-13, with the simultaneous application of Trilon B as a masking complexing agent.

4. Another four dyes were prepared from diazotized H-acid, by combining it with various substituted α-naphthols, including H-acid itself; a study of these dyes showed that the product formed by combining diazotized H-acid with H-acid, and which we called Berillon I (X), is also of interest as a reagent for the colorimetric determination of beryllium and cobalt.

5. On the basis of the experimental data obtained, it was established that the group ortho-hydroxy-peri-hydroxy'-2,1'-azonaphthalene (VII) is less characteristic for Be, than peri-dihydroxy-ortho-azo, and that the properties which are of practical value are possessed to the highest degree by a compound which contains both groups at the same time, i.e., Compound (VI) – Berillon II.

LITERATURE CITED

[1] V. Caglioti, Chem. Zentr. 1927, II, 1739.

[2] L. Moser and M. Niessner, Monatsh. 48, 113 (1927).

[3] M. L. Nichols and I. M. Schempf, Ind. Eng. Chem., Anal. Ed. 11, 278 (1939).

[4] J. H. Yoe and W. L. Hill, J. Am. Chem., Soc. 49, 2395 (1927).

[5] G. E. Kosel and W. F. Neuman, Anal. Chem. 22, 936 (1950).

[6] L. M. Kolthoff, J. Am. Chem. Soc. 50, 393 (1928).

[7] H. Fischer, Z. anal. Chem. 73, 54 (1928).

[8] L. P. Adamovich, Trans. Sci. Research Inst. of Kharkov State University (1951), Vol. 8, p. 9.

[9] S. Ato, Chem. Zentr. 1931, I, 1484,

[10] A. S. Komarovsky and N. S. Poluetkov, J. Appl. Chem. 7, 839 (1934).

---

* These were taken by Yu. I. Pecherskaya.

[11] F. A. Vinci, Anal. Chem. 25, 1580 (1953).

[12] L. P. Adamovich, Trans. of the Chemistry Faculty and the Sci. Research Institute of Kharkov State University (1954), Vol. 12, p. 167.

[13] J. V. Dubsky and E. Krametz, Mikrochemie 20 (N. F. 14), 57 (1936).

[14] A. L. Underwood and W. F. Neuman, Anal. Chem. 21, 1348 (1949).

[15] T. Y. Toribara and A. L. Underwood, Anal. Chem. 21, 1352 (1949).

[16] A. L. Underwood, T. Y. Toribara and W. F. Neuman, J. Am. Chem. Soc. 72, 5597 (1950).

[17] E. B. Sandell, Ind. Eng. Chem., Anal. Ed. 12, 762 (1940).

[18] C. E. White and C. S. Lowe, Ind. Eng. Chem., Anal. Ed. 13, 809 (1941).

[19] M. H. Fletcher, C. E. White and M. S. Sheftel, Ind. Eng. Chem., Anal. Ed. 18, 179 (1946).

[20] W. N. Aldridge and H. F. Liddell, Analyst 73, 607 (1948).

[21] M. W. Cucci, W. F. Neuman and B. I. Mulryan, Anal. Chem. 21, 1358 (1949).

[22] H. V. Meek and C. V. Banks, Anal. Chem. 22, 1512 (1950).

[23] H. V. Meek and C. V. Banks, J. Am. Chem. Soc. 73, 4108 (1951).

[24] I. S. Mustafin and L. M. Kulberg, Ukrain. Chem. J. 19, 421 (1953).

[25] S. I. Barskaya and F. M. Shemyakin, Factory Lab. 19, 160 (1953).

[26] L. P. Adamovich and R. S. Didenko, Trans. of the Chemistry Faculty and the Sci. Research Institute of Kharkov State University (1954), 12, p. 195.

[27] Z. Holzbecher, Collection of Czechoslovak Chem. Papers 20, 192 (1955).

[28] I. H. Wood, Mikrochim. Acta, 1955, p. 11.

[29] E. B. Sandell, "Colorimetric Determination of Metal Traces" (State Chem. Press, 1949), p. 559.

[30] G. Heller, Ber. 50, 1247 (1917).

[31] C. Brenner, Helv. Chim. Acta, 3, 90 (1920).

[32] A. S. Komarovsky and N. S. Poluetkov, J. Appl. Chem. 7, 841 (1934).

[33] N. S. Poluetkov, J. Appl. Chem. 9, 164 (1936).

[34] V. I. Kuznetsov, J. Gen. Chem. 14, 902 (1944).

[35] V. I. Kuznetsov, Proc. Acad. Sci. USSR 50, 227 (1945).

[36] V. I. Kuznetsov, Proc. Acad. Sci. USSR 52, 39 (1946).

[37] V. I. Kuznetsov, J. Anal. Chem. 2, 69 (1947).

[38] V. I. Kuznetsov, Proc. Acad. Sci. USSR 59, 501 (1948).

[39] V. I. Kuznetsov, J. Anal. Chem. 3, 295 (1948).

[40] V. I. Kuznetsov and L. S. Kozyreva, J. Anal. Chem. 8, 90 (1953) (T. p. 101).*

[41] V. G. Goryushina, Factory Lab. 19, 300 (1953).

[42] S. Ya. Shneiderman, Ukrain Chem. J. 19, 327 (1953).

[43] S. Ya. Shneiderman and N. P. Movchan, Ukrain. Chem. J. 9, 429 (1953).

[44] V. M. Rodionov, B. M. Bogoslovsky and A. M. Fedorova, "Laboratory Textbook on the Chemistry of Intermediate Products and Dyes" (State Chem. Press, 1948), p. 212.

[45] P. Molau and G. Bukherer, "Practical Textbook on the Chemistry of Dye-Stuffs"(Chemico-Technical Press, 1927), p. 414.

[46] M. A. Chekalin and F. F. Ererin, "The Production of Azo Dyes"(State Chem. Press, 1952), p. 448.

[47] R. Pribil and I. Kucharsky, Collection trav. chim. Tchecoslov, 15, 132 (1950).

[48] A. M. Lukin, G. G. Karanovich and G. B. Zavarikhina, Author's Thesis, No. 101688 for 9.07.1954.

[49] G. G. Karanovich, J. Anal. Chem. 11, 400 (1956) (T. p. 417).*

[50] N. S. Poluetkov and M. P. Nikonova, Trans. Commission on Analytical Chemistry, Vol. III (VI) (Acad. Sci. USSR Press 1951), p. 188.

Received August 8, 1955

---

* T. p. = C. B. Translation pagination.

COLORIMETRIC DETERMINATION OF BERYLLIUM BY MEANS OF A NEW REAGENT – BERILLON II

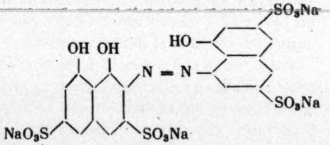
G. G. Karanovich

All-Union Scientific Research Institute for Chemical Reagents, Moscow

Of the limited number of reagents which have been suggested for the colorimetric determination of small amounts of beryllium, quinalizarin is one of those which is widely used in analytical practice (quinalizarin is 1, 2, 5, 8-tetrahydroxyanthraquinone) [1, 2]. This reagent forms a blue colored compound with beryllium in alkaline media. Under the same conditions, but in the absence of beryllium, the quinalizarin solution remains violet. Aluminum and metals which are soluble in excess sodium hydroxide do not interfere with the determination of beryllium. The drawback of this reagent is its low stability in alkaline media [1].

We have made a study* of a new reagent for beryllium; this was synthesized in the Institute for Chemical Reagents, and has been suggested as a reagent for beryllium by Lukin and Zavarikhina [5, 6].

The azo compound which the authors obtained by combining chromotropic acid with diazotized H-acid, has been called Berillon II, and which we shall henceforth refer to as Berillon for the sake of brevity, is a highly sensitive reagent for beryllium. Aqueous solutions of the reagent are violet-red when the medium is acid or neutral, while alkaline solutions are violet. A solution of the reagent forms colored compounds with various elements at different pH values (Table 1). Ba, Li, Pb, Cd, Zn, As, Hg^{2+}, Sn^{II}, Sb^{III}, W, V, Os, Pr, Na and K do not form colored compounds at pH from ~1-13.



[8-hydroxynaphthalene-3,6-disulfonic acid-(1-azo-2') -1',8'-dihydroxynaphthalene-3',6'-disulfonic acid, tetrasodium salt]

A 0.02% aqueous solution of the reagent and standard beryllium solutions ($BeSO_4 \cdot 4H_2O$), containing 1, 0.01 and 0.001 mg/ml of Be, were used for beryllium determination. In order to establish optimum conditions, we considered it expedient to ascertain the indicator properties of the test azo dye, so that determination of beryllium should be carried out in the region where the color of the indicator is most stable. This pH region, depending on the properties of the metal to be determined, may be below the transition interval of the dye or above it. By observing the color changes with pH, we established that the transition range (interval) from red to violet extends over pH ~ 9.2 to 10.6. A stable violet color is observed up to a pH of ~14. In more alkaline solutions, the violet color changes to a red-violet (characteristic of neutral or weakly acid media).

---

* V. G. Savchenko and B. L. Lerner participated in the experimental work.

TABLE 1

Formation of Colored Compounds

Element	pH	Color of reagent	Color with the element	Element	pH	Color of reagent	Color with the element
Ca	10.8—14	Violet	Dark blue	Cu	8.0—14	Violet	Blue
Mg	9.6–14	Violet	Dark blue	Ni	8.8—13	Violet	Dark blue
Be	5.1—6.2	Rose	Blue	Co	9.0—14	Violet	Blue
Be	11.5—14	Violet	Blue	Mn^{2+}	9.6	Violet	Dark blue
Al	5	Rose	Violet	Mo	12	Violet	Dark blue
Al	11	Violet	Dark blue	Cr^{3+}	11—13	Violet	Blue-violet
Fe^{+3}	5.6	Rose	Brown				
Fe^{+3}	7.6	Rose	Brown	Sc	4—6	Rose	Blue
Cu	6.0	Rose	Dark blue	Th	4—6	Rose	Blue
				Pd	11—14	Violet	Blue

In trying to find out the effect of pH on the intensity of the color developed during interaction of the reagent with beryllium, we established that the composition of the buffer mixture is of great significance. Thus, with urotropine at a pH of 5.1-5.8, we observed a clear-cut color (reaction sensitivity 0.2 γ Be in 5 ml solution). With an acetate buffer (pH ~ 5.2-5.6) however, we could not get good results.

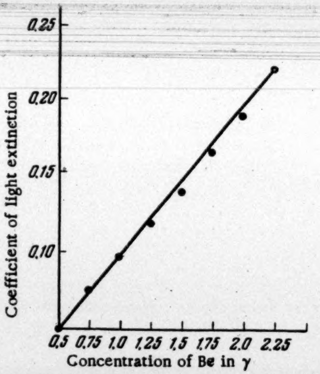


Figure 1. Relation between color and beryllium concentration in solution.

According to published results, beryllium is determined colorimetrically in the presence of aluminum in a sodium hydroxide medium with the help of quinalizarin. It was established experimentally that at a pH of ~12-13.2, a clear-cut color can be observed during the reaction of Berillon with Be. The sensitivity of the reaction is 0.2 γ Be in 5 ml of solution. The color achieves its maximum intensity after 2 minutes, but it is more convenient to make measurements after 5 minutes. The color is stable for 18 hours. Photocolorimetric determination (at 600 m μ) showed that the relation between color intensity and amount of beryllium in solution is linear within a narrow concentration range (Fig. 1).

Into test tubes containing 0.1, 0.2, 0.5, 1, 2, 4, and 5 γ of Be respectively in 2 ml of water, and one test tube containing 2 ml used as a control (free from beryllium) was added water to bring the volume up to 4.25 ml. 0.2 ml of 10% NaOH and 0.5 ml of 0.02% Berillon solution respectively were added to each of the test tubes. The control solution was colored violet, while in the test solutions, the color varied with the beryllium content, from blue-violet (2 γ Be), through dark blue (4 γ Be), to blue (6 γ Be).

The color developed when 0.2 γ of Be is present can still be observed quite distinctly.

In ammoniacal media (pH ~11.6), a non-contrasting scale is obtained, and the sensitivity drops (4 γ Be in 5 ml solution). In subsequent experiments, determination of beryllium was accordingly carried out in sodium hydroxide (pH ~ 12-13.2), particularly when it was determined in the presence of aluminum.

Table 2 contains data on the limiting concentrations of other elements (as well as Na).

TABLE 2

Determination of Beryllium in the Presence of Other Elements

Beryllium		Relative error in %	Me in mg	Ratio Be : Me
Introduced in γ	Found in γ			
0,5	0.5	0	Pb 1.0	1 : 2000
1.0	1.0	0		
2.0	1.8	—10		
0.5	0.5	0	Cd 0.1	1 : 200
2.0	2.2	+10		
1.0	1.1	+10	Zn 0.5	1 : 500
0.5	0.5	0	As 1.0	1 : 2000
4.0	3.9	— 3		
0.5	0.5	0	Hg^{2+} 0.5	1 : 1000
1.0	1.0	0	Ba 0.2	1 : 200
1.0	1.1	+10	Zi 0.5	1 : 500
1.0	0.95	— 5	W 0.1	1 : 100
2.0	2.1	+ 5	V 0.1	1 : 50
0.5	0.5	0	Na 4.0	1 : 8000

We established that Ca, Mg, Al, Fe^{3+}, Cu, Ni, Co, Mn, Mo and Cr^{III} form colored compounds with the reagent in the pH range which is most favorable for beryllium determination (see Table 1).

It was found however that they do not interfere with Be determination at the following concentrations: up to 25 γ Fe, up to 200 γ Al, up to 15 γ Mg, up to 4 γ Ca, and up to 10 γ Ni; greater amounts of these elements, and also Co, Cu, and Cr^{III} (in amounts of 1 γ and more) distort the results of beryllium determination strongly. In order to eliminate interference from these elements on the accuracy of beryllium determination, Trilon B was used. Trilon B forms, under the conditions used for beryllium determination – viz. a pH of ~ 12-13.2 – stable complexes with all the cations listed above (apart from iron), and does not change the color of the compound formed with beryllium. When the metals listed above are present, the procedure adopted is as follows: to 3 ml of test solution containing from 0.5 to 6 γ Be and 50 γ Cu (or another metal in amounts up to 400 γ), is added 0.5 ml of a 5% solution of Trilon B, 0.2 ml of a 10% sodium hydroxide solution, 0.5 ml of a 0.02% solution of Berillon, and the volume made up to 5 ml with water.

The color which develops is compared after 5 minutes with a series of standard solutions (also containing the same amount of Trilon B, see Table 3) or the intensity is measured on a photocolorimeter (at 600 mμ).

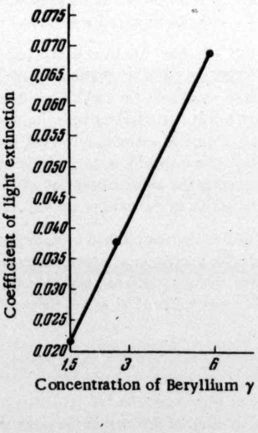


Figure 2. Colorimetric determination of beryllium in the presence of aluminum.

We did not succeed in complexing iron as a stable complex by the use of various complexing agents. Best results were obtained after reducing it with ascorbic acid; nevertheless, a large excess destroys the color of the beryllium complex and the reagent. To reduce 100 γ of Fe^{3+} it is sufficient to add 0.25 - 0.3 ml of 5% ascorbic acid before addition of alkali; this same amount of ascorbic acid is also added to the standards. Under these conditions, the reaction sensitivity for beryllium drops somewhat.

TABLE 3

Determination of Beryllium in the Presence of Ni, Co, Cu, Mg and Ca After Masking Trilon B and After Reducing Fe^{3+} with Ascorbic Acid

Me taken in mg	Beryllium		Error in γ	Me taken in mg	Beryllium		Error in γ
	Introduced in γ	Found in γ			Introduced in γ	Found in γ	
Ni 0,5	0.5	0.5	0	+ Ca 0.4 Mg 0.4	0.5	0.5	0
	1.0	1.0	0		1.0	1,1	+0.1
	2.0	2.1	+0.1		4.0	4.2	+0.2
Co 0,5	1.0	1.0	0	Fe^{3+} 0.05	4.0	4.0	0
	4.0	4.2	+0.2		8.0	8.4	+0.4
Cu 0,05	0.5	0.5	0		16.0	15.0	—1
	6.0	5.7	—0,3				
Mg 0,4	0.5	0.5	0				
	1.0	1.0	0				
Ca 0,4	2.0	2.0	0				
	4.0	3.8	—0.2				

It was stated above that beryllium can be determined in 5 ml of solution in the presence of aluminum at a ratio of Be : Al = 1 : 200; greater amounts of aluminum lead to high results. Only 8-hydroxyquinoline proved successful for complexing aluminum. This complex remains stable in a solution of sodium hydroxide at a pH of ~12-13.2. Under these conditions it is possible to determine beryllium at ratios of Be : Al = 1 : 500.

For higher amounts of aluminum, considerably more of the 10% solution of sodium hydroxide (2-2.5 ml instead of 0.25 ml) is used for dissolving the aluminum complex. This increase in alkalinity leads to a breakdown of the aluminum hydroxyquinolate and to a decrease in reaction sensitivity for beryllium. Nevertheless, at this appreciably high alkalinity, aluminum remains in solution and does not interfere with the determination of beryllium, but the sensitivity drops. For the determination of beryllium in aluminum sulfate, and in potash alum, one can start with a sample weight of ~0.025 g of the final volume should be 10 ml, containing ~2 - 2.5 ml of 10% sodium hydroxide (the solution should be clear). Exactly the same amount of alkali should also be added to the standard solutions as was used for dissolving the precipitate in the case of the test solution.

Rapid development of the color permits one to determine beryllium by the method of colorimetric microtitration. The capacity of the reagent to form a colored compound with beryllium at appreciable salt concentrations, permits beryllium to be determined in solutions of the acetates, sulfates, nitrates, and chlorides of the alkali metals at a pH of ~ 12-13.2. Ammonium salts, however, in concentrations at which they can affect the pH of the solution, should be absent.

SUMMARY

1. An azo compound obtained by combining chromotropic acid with diazotized H-acid, forms with beryllium a blue colored compound which is stable for 18 hours. An aqueous solution of this reagent is more stable than an aqueous solution of quinalizarin.

2. The reagent has a similar sensitivity to quinalizarin (0.2 γ Be in 5 ml of solution).

3. Conditions have been worked out for determination of beryllium in the presence of Fe^{3+}, Co, Ni, Cu, Al, Mg, and Ca.

LITERATURE CITED

[1] E. B. Sandell, "Colorimetric Determination of Metal Traces" (State Chem. Press, 1949), pp. 154-157.

[2] "Reactions and Reagents for Qualitative Analysis of Inorganic Compounds", Edited by A. S. Komarovsky, 1950, pp. 133-135,

[3] A. S. Komarovsky and N. S. Poluetkov, J. Appl. Chem. 7, 839 (1934).

[4] A. L. Underwood, T. V. Toribara and W. F. Neuman, J. Am. Chem. Soc. 72, 5597 (1950).

[5] A. M. Lukin, G. G. Karanovich and G. B. Zavarikhina, Author's Thesis No. 101688 of 7/9/1954.

[6] A. M. Lukin and G. B. Zavarakhina, J. Anal. Chem. 11, 393 (1956) (T. p. 409).*

Received August 26, 1955

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

NEW COMPLEXONES

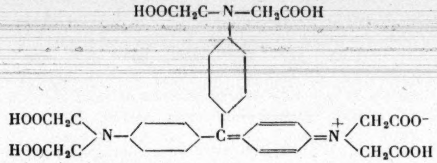
PART II. PARAFUCHSINHEXAACETIC ACID*

R. P. Lastovsky, Yu. I. Vainshtein, N. M. Dyatlova and V. Ya. Temkina

All-Union Scientific Research Institute for Chemical Reagents, Moscow

Of great interest is the preparation of colored compounds of the complexone type, which can be used for colorimetric determination, and as indicators in complexometric titration. Phthalein complexone which has been described in the literature [2], is of this type.

We have synthesized parafuchsinhexaacetic acid which has not yet been described in the literature; apparently, it has the following structure:



Synthesis of Parafuchsinhexaacetic Acid

It was synthesized by condensing parafuchsin with sodium mono-chloroacetate. 10 g of parafuchsin in 500 ml of water is heated to 80° and a solution of 90 g of mono-chloroacetic acid, previously neutralized with 5 N alkali, added. The reaction is carried out at a temperature of 100° and a pH of 8-10 for 3 hours. When the reaction has finished, the mixture is cooled and filtered. The filtrate is acidified with hydrochloric acid until the solution is acid to methyl orange. The dye which settles out is filtered off, dissolved in 1 N alkali, precipitated with acid, and recrystallized from water. The final product is a violet crystalline powder which is soluble in alkalis, sparingly soluble in alcohol and hot water, and practically insoluble in cold water.

Analytical Results

Found % C 58.68, 58.88; H 5.19, 5.11; N 6.57, 6.68. Calculated for $C_{30}H_{29}N_3O_{12}$%: C 58.58; H 4.72; N 6.61.

---

* For Part I, see [1].

In order to characterize the compound thus prepared, absorption curves of its solutions were taken at pH of 1 and 9 respectively; these are shown in Fig. 1.

At pH 1, λ_{max} = 585 mμ; at pH 9, λ_{max} = 560 mμ. According to published results for parafuchsin [3], at pH 1, λ_{max} = 487 mμ, and at pH 9, λ_{max} = 543 mμ.

Indicator Properties of Parafuchsinhexaacetic Acid

Parafuchsinhexaacetic acid exhibits the properties of an acid-base indicator with two color changes. The first is observed at pH 2.2-4.2 from rose to violet; the second, at a pH of 11.8 - 13.4 from violet to colorless. It should be noted that on standing for 8-10 minutes, the solution will become colorless even at a pH of 13.0. A 0.1% aqueous solution of the trisodium salt of parafuchsinhexaacetic acid (this is prepared by dissolving an aliquot of the acid in the calculated amount of 0.1 N sodium hydroxide) is used as an indicator solution.

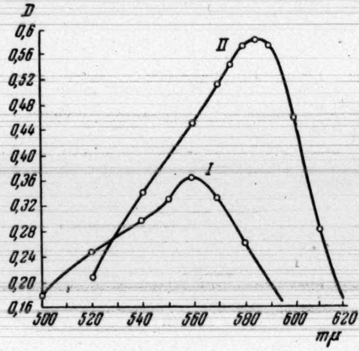


Figure 1. I) Absorption curve for a solution of parafuchsinhexaacetic acid at a pH of 1. Concentration of solution, 1 mg in 100 ml water. II) Absorption curve for a solution of parafuchsinhexaacetic acid at a pH of 9. Concentration of solution, 1 mg in 500 ml water.

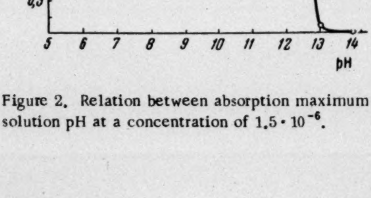


Figure 2. Relation between absorption maximum and solution pH at a concentration of $1.5 \cdot 10^{-6}$.

It was shown during a spectrophotometric study of a solution of parafuchsinhexaacetic acid, that at pH of 5-13, there is observed a constant absorption maximum which lies between 580 and 585 m μ. The curve relating absorption to solution pH, and constructed for the indicated pH range, reflects color change well (Fig. 2).

Analytical Study of Parafuchsinhexaacetic Acid

It has been established,* that the violet color of an alcohol solution of parafuchsinhexaacetic acid changes to rose on addition of Fe^{3+}, Ag^{+}, Hg^{2+}, Cd^{2+}, Mo^{VI}, Al^{3+}, Be^{2+}, La^{III}, V^{V}, Zn^{2+}, and Ca^{2+} at pH 4.6-5.8. Lead forms a bright red complex. Cu^{2+}, Ni^{2+}, Cr^{3+}, and Mn^{2+} ions do not give a color change.

For detecting lead, it is convenient to use a buffer solution of succinic acid and borax (pH 5.8). A spot technique (paper chromatography) permits determination of 0.2 γ Pb^{2+} in one micro-drop. Fe^{3+}, Cd^{2+}, Ag^{+}, Hg^{2+}, La^{III}, Al^{3+}, Ca^{2+} interfere with detection of lead; Cu^{2+}, Ni^{2+}, Cr^{3+}, and Mn^{2+} do not.

Polarographic Study of Parafuchsinhexaacetic Acid

In order to find out some information about the complexing properties of parafuchsinhexaacetic acid, and for the purpose of using it in chemical analysis in future, this compound was studied polarographically.

In order to get an estimate of the stability of the complexes formed, we chose, as before, in our first communication, the polarographic method of determining the shift in the half-wave potential for certain cations in the presence of the complexone. In a number of instances, during reaction of the complexone with some cations, equilibrium is not established instantaneously, but takes some time; accordingly, test solutions were examined polarographically, immediately after their preparation; after the solution had stood in the dark at room temperature for 5 days; and, finally, after 15 days. In all, 16 cations were tested. For these tests a 0.01 M solution of the complexone was used; this was prepared by dissolving 0.635 g of the preparation in 100 ml of 0.1 N NaOH. The following buffer mixture was used:

Solution 1 (pH 2.5) – 0.4 M solution of acetic acid
Solution 2 (pH 4.4) – 0.4 M solution of acetic acid + 0.4 M solution of sodium acetate
Solution 3 (pH 9.35) – 0.1 M solution of ammonium hydroxide + 0.1 M solution ammonium chloride
Solution 4 (pH 12.4) – 0.1 M solution sodium hydroxide

Test solutions were prepared as follows: into a 100 ml standard flask were introduced 10 ml of 0.01 M complexone solution, 1 ml of 0.1 % gelatine solution, the test cation in an amount corresponding to a final concentration of $1 \cdot 10^{-4}$ M, and the whole made up to the mark with the respective buffer. Polarograms were taken immediately after preparing the solutions, and also after 5 days and 15 days standing, respectively. After 5 days standing, no further changes in $E_{1/2}$ were observed.

Polarograms were taken on a Heirovsky type polarograph after preliminary bubbling of hydrogen through the solutions for 15 minutes. A dropping mercury electrode on which the drops are artificially forced off was used as a cathode, while the anode was a saturated calomel electrode. The table contains results for the half-wave potentials of the various cations both in the absence and in the presence of the complexone respectively.

It follows from these results that on addition of parafuchsinhexaacetic acid to a solution of a test cation, the the half-wave potentials are displaced to varying amounts, thereby indicating varying stabilities of the complexes formed.

Lead. At a pH of 2.5, on addition of lead, the solution remains clear, but after 5 days a precipitate forms. Wave height for lead drops with time. At a pH of 3.2, on introducing lead into a solution of parafuchsinhexaacetic acid, a precipitate forms immediately and the solution becomes colorless. No lead could be detected in the filtrate. At a pH of 4.4, complex formation occurs with time, and equilibrium is attained after the solution has stood for 5 days. The half-wave potential shifts from –0.43 to –0.80 V. Similar behavior is observed at a pH of 9.35. At pH 12, formation of the complexonate of parafuchsinhexaacetic acid occurs; its reduction proceeds stepwise; the first step which is clearly defined occurs at a half-wave potential of $E_{1/2} = -0.45$ V and extends to $E_{1/2} = -1.10$ V. Addition of parafuchsinhexaacetic acid does not lead to a drop in the height of the first wave; this indicates that this wave is not connected with reduction of sodium biplumbite or a simple lead cation:

---

* According to G. G. Karanovich's results.

TABLE

Half-Wave Potentials of Various Cations in the Presence of Parafuchsinhexaacetic Acid, Measured Against the Saturated Calomel Electrode (in Volts)

Ions	pH 2,5			pH 4.4			pH 9,35			pH 12		
	Without the complexone	In the presence of the complexone	In the presence of the complexone after standing 5 days	Without the complexone	In the presence of the complexone	In the presence of the complexone after standing 5 days	Without the complexone	In the presence of the complexone	In the presence of the complexone after standing for 5 days	Without the complexone	In the presence of the complexone	In the presence of the complexone after standing for 5 days
Pb^{2+}	—0.38	—0.40	A precipitate forms	—0.43	—0.43	—0.80	—0.18	—0.40	—0.60	—0.7	—1.10 —0.45	No change
Cu^{2+}	+0.02	disappears	No change	—0.02	—0.84	No change	—0.29 —0.54	—0.58	No change	—0.05	—0.05 —1.18	»
Bi^{3+}	—0.12	»	»	—0.21	—0.16 —0.82 —1.12	»	—	—0.60 —0.20	—	—0.71	—0.7	»
Cd^{2+}	—0.60	—0.64	»	—0.62	—0.6 —0.82	»	—0.62	—0.68	—	—	—0.8	—1.02
Tl^{+}	—0.46	Precip.	»	—0.46	disappears	»	—0.48	—0.48	—0,42 —0,62	—0.46	—1,21	—0.4 —0.92
As^{III}	—1.02	—0.52 —1.18	»	—	—0.82	»	—1.70	—0.52 —1.26	—0,58 —1,20	—	—1,00	No change
Sb^{III}	—0.19	—0.26	»	—0.38	—0.19	»	—	—0.19	No change	—1.17	—0.21 —1.17	»
Sn^{II}	—0.02 —0.30	disappears	»	—0.17 —0.50	disappears	»	—	—0,52	»	—	—1.20	»
Zn^{2+}	—1.08	—1.08	»	—1.09	—0.82	»	—1.18	—1.22	»	—1.47	—	»
Ni^{2+}	—1.02	disappears	»	—1.12	—0.82	»	—1.01	—0.65	—0,60	—1.37	—1.16	»
Co^{2+}	—1.12	»	»	—1.15	—0.81	»	—1.21	—1.20	—0,66	—1.37	—1.37	—1.06
Mn^{2+}	—	—	»	—1.50	—0.82	»	—1.58	—1.12	No change	—	—1.34	No change
Fe^{III}	—	—	»	—1.36	—0.82	»	—	—1.15	»	—	change in color of solution	»
Cr^{III}	—	—	»	—0.89 —0.51	—0.9	»	—1.56	—0,1 —1.2	»	—	—1.35	»
Mo^{VI}	—0.52	—0.47	»	—0.24 —0.64	—0.8	»	—	—	—	—	—	—
Ti^{IV}	—0.65 —0.97	disappears	»	—	—0.96	»	—	—1.25	—	—	—	—
La^{III}	—0.62	—0.78	»	—0.72	—0.72	»	—0.68	—0.89	—	—	—	—

Note. Al^{3+}, Th^{4+}, Be^{2+}, W^{VI} are not reduced under the test conditions.

its appearance is determined by the formation of a complexonate; the other wave appears, presumably, as the result of the formation of a hydroxy-complex, this is confirmed by the fact that it disappears at pH 2.5 and 4.7.

Copper. A stable complex is formed, since the reduction wave disappears at pH 2.5. Similar behavior with other known complexones is not observed. At pH 4.4 a shift in the half-wave potential of copper to −0.84 V is observed; this should allow one to determine elements which are reduced at less negative potentials than copper, in the presence of copper.

Bismuth. At pH 2.5 and 4.4, bismuth forms stable complexes.

Thallium. Forms a very stable complex; at pH 4.4 the wave disappears. At pH 9.35 thallium complexonate is again formed. Such behavior is not observed with other known complexones.

Tin. At pH 2.5 and 4.4, very stable complexes are formed.

Iron. At pH 4.4 and 12, stable complexes are formed.

As is evident from the table, parafuchsinhexaacetic acid forms complexes with most of the test cations. Of special interest from a practical point of view are the complexonates of those cations, with which other known complexones [4], do not form complexes under analogous conditions. The possibility of using parafuchsinhexaacetic acid as an indicator for complexometric titration, and for colorimetric determinations, is being investigated.

SUMMARY

1. Parafuchsinhexaacetic acid has been synthesized and characterized.

2. The complex-forming and indicator properties respectively of the compound prepared have been investigated.

3. It has been shown that parafuchsinhexaacetic acid may be of potential use in polarography.

LITERATURE CITED

[1] R. P. Lastovsky, Yu. I. Vainshtein, N. M. Dyatlova, N. M. Temkina, and I. D. Kolpakova, J. Anal. Chem. 10, 128 (1955) (T. p. 117).*

[2] G. Anderegg, H. Flaschka, R. Sallmann and G. Schwarzenbach, Helv. Chim. Acta 37, 113 (1954).

[3] Color Index, 1924, p. 172.

[4] R. Pribil, Komplexony v chemicke analyse, 1953.

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

EFFECT OF THE BULK COMPOSITION OF A MINERAL ON RESULTS OF THE QUANTITATIVE DETERMINATION OF MOLYBDENUM IN GRANITOIDS

E. E. Vainshtein and L. I. Pavlenko

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow

Investigation of the effect of the bulk composition of a material on the results of spectrographic analysis is, as is well known, one of the most important problems in the field of analytical chemistry. The fact that such an influence does exist, puts a limit on the universal applicability of spectrographic methods which have been developed; it also acts unfavorably on the accuracy and reliability of an analysis. The complexity of the phenomena and the insufficiently developed state of many points in the theory of spectrographic analysis makes it difficult to forecast and evaluate quantitatively the direction and magnitude of this effect. It is only possible to draw such conclusions on the basis of an analysis of the results of experimental work which has been carried out systematically.

In the present article we have described the results of a study of the effect of the bulk composition of a mineral on the results of the quantitative determination of molybdenum in granitoids (granites, granodiorites) and diorites, and a simple method which has been developed for calculating this effect.

Experimental Procedure and Calibration Curves for Determining Molybdenum in Granitoids

The molybdenum content of granitoids was determined on the Qu-24 quartz spectrograph. The spectrograph slit was illuminated with a three lens condenser. Slit width was 0.02 mm. The source was a D. C. arc with carbon electrodes of the usual form having a 5 mm cavity. The well-ground-up test sample, or standard, weighing 20 mg was placed in the cavity of the carbon electrode serving as anode, and evaporated completely in the course of 45 minutes. For the first 30 seconds the current was kept at 6 amp; for the subsequent 4 minutes it was kept at 10 amp. Molybdenum was determined quantitatively by means of the 3170.35 A line. Spectra were photographed on "Spectrographic Type II" plates with a sensitivity of 8 units on the GOST scale. The standards used in this investigation were prepared from granite rocks which, according to analytical results, did not contain appreciable amount of molybdenum. The fact that it is uncertain as to the chemical form the molybdenum assumes in granitoids [1], and the well known dependence between the character of the evaporation curve for an element and the chemical composition of the compound in which it is found in the test material [2], made it desirous to carry out an experimental verification of the suitability

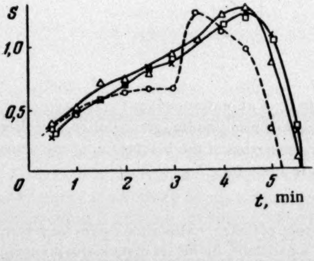


Figure 1. Curves for the evaporation of molybdenum from granite (△) and standards prepared from molybdenum which has been introduced into the mineral as MoO_3 (o), MoS_2 (x) and MoS_3 (□).

of various molybdenum compounds for their use for preparing standards. In this connection therefore the nature of the evaporation of molybdenum from synthetically prepared standards, into which it was introduced as the oxide or sulfides (molybdenite – MoS_2, and the reagent MoS_3), was studied. Curves for the evaporation of molybdenum directly from granitoids, and from standards containing Mo in the form of sulfides are identical (Fig. 1). Evaporation of molybdenum from standards into which it had been introduced as the oxide, proceeds somewhat differently.* Accordingly, in subsequent work standards were prepared by triturating molybdenum as molybdenite (MoS_2) or the chemically pure reagent MoS_3, with the base material. The molybdenum content of the standards was varied within the range 10^{-4} to $7 \cdot 10^{-2}$ %.

Three series of standards were prepared which corresponded respectively to granite, granodiorite, and diorite bases. The contents of the principal components, sodium and potassium, in the rocks used for preparing the standards, were determined spectrographically, using a method described previously [3, 4]. The values thus obtained are given in Table 1.

TABLE 1

Composition of Granitoids Used for Preparing Standards

Type of ore	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O
Granite	73,5	15,3	1,7	2,1	0,6	3,15	4,90
Granodiorite	66,6	18,7	3,3	5,3	1,6	3,10	3,25
Diorite	58,5	19,5	7,6	8,5	4,9	3,10	2,15

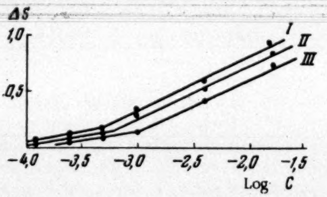


Figure 2. Calibration curves for determination of molybdenum in granite I, granodiorite II, and diorite III in the coordinates (ΔS, log C).

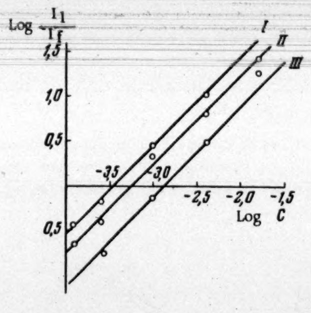


Figure 3. Calibration curves for determination of molybdenum in granite, granodiorite, and diorite after conversion of the blackening of molybdenum lines to intensity.

Calibration curves were constructed by means of the three standards method. Blackening of the analytical line of the test element was compared with blackening of the spectrogram background. On Fig. 2 are given a group of typical calibration curves for determination of molybdenum, which have been drawn within the coordinates ΔS, logarithm C by means of standards prepared on the basis of granite (I), granodiorite (II), and diorite (III). The same curves are given in Fig. 3 after conversion to intensities. It it evident that the method of analysis described permits one to determine molybdenum quantitatively in granitoids for contents of the element exceeding 10^{-4} %. All three curves have an exactly similar shape. Nevertheless, on switching from granite to diorite, the curves, while remaining parallel, are displaced uniformly with respect to one another.

---

* As shown experimentally, this is reflected in the parallel displacement of the calibration curves (ΔS, log C), constructed on the basis of standards containing Mo as the oxide and sulfides respectively.

Conditions for Excitation and Evaporation of Molybdenum from Granitoids in a D. C. Arc

In order to find out the reasons for the displacement of the calibration curves during determination of molybdenum in granitoids and diorite, a systematic investigation of the conditions for excitation and evaporation of the elements from the minerals was carried out. The method adopted differed from that generally used, and was based on the use of marked atoms; it permitted the process of evaporation and excitation of the atoms in the source to be studied independently. The true evaporation curve of the test element from the mineral was found experimentally by means of the marked isotope of this element. At the same time, spectrograms were registered on a moving plate, treatment of which allows one, by the usual method, to construct curves for changes in intensity of the analytical lines of the element during exposure. Results obtained by consideration of both curves, permits one to have an idea of the changes in conditions of excitation of the atoms of the element. In the work described here, the radioactive isotope Mo^{99} with a half-life of 2.8 days was used. Radiation intensity of the β-activity was recorded by using a torsion counter. During the β-discharge, an equilibrium is established between Mo^{99} and the Tc^{99} formed from it. The fact, which we showed experimentally, that curves for changes in activity of mixtures of Mo and Tc with time, before and after evaporation in the arc (Fig. 4), do not vary, indicates the absence of any appreciable fractionation of these elements, and permits one to disregard the presence of Tc atoms in the marked preparation used.

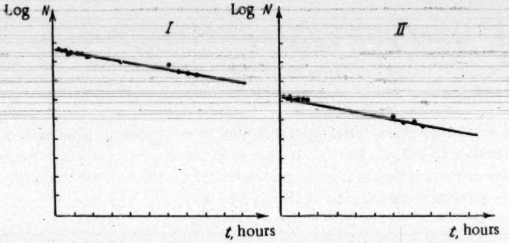


Figure 4. Curves for changes in activity of Mo^{99} and Tc^{99} found in equilibrium with it, with time: I) before evaporation in the arc; II) after evaporation in the arc for 1.5 minutes.

Experiments were carried out as follows. The marked isotope Mo^{99} as MoS_3 was introduced into one of the standards prepared from granite, granodiorite, and diorite, respectively. Afterwards, each of the materials charged with isotope was weighed out in 10 sample lots (20 mg each), and after the activity of each had been measured, they were placed in the cavities of ten electrodes exactly identical in size. Each electrode was then ignited for various times, varying from 30 seconds to 3.5 minutes, under standard conditions, described in the previous section. The activity of any unburnt powder was next measured, and the percentage evaporation of molybdenum atoms with time calculated. The results of these calculations are represented graphically. The reproducibility of the measurements described was calculated from results of five parallel tests. The mean arithmetic error of a single determination was found to be ± 5%. At the same time as the true curve for evaporation of molybdenum from the mineral was being constructed, the intensity of the analytical line of the element with time of arc burning was registered. For convenience of comparison of this last curve with the evaporation curve, the intensity of the line for Mo (I) on the spectrograms is represented as a fraction of the maximum intensity of the line of the element after its practically complete evaporation from the mineral (I_{max}).

The experimental evaporation curves obtained in this way, and the curves characterizing change in intensity of the Mo line with time during its evaporation in a D. C. arc, from granite I, and diorite II, e.g., are shown in Fig. 5 (a and b). Here (Curves c) are depicted curves which represent the quotient from division of the first group of curves into the other; they characterize the change in conditions of excitation of molybdenum atoms in the arc.

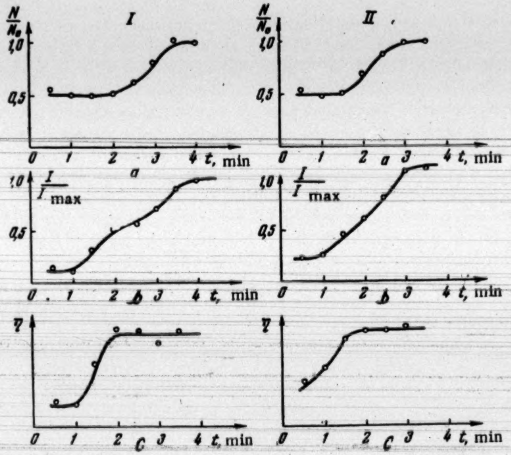


Figure 5. Curves characterizing evaporation of molybdenum from granite I, and diorite II in a D. C. arc: a) evaporation curves; b) relation between intensity of the analytical line for molybdenum and time of arc burning; c) η – quotient from division of Curves b by a.

Consideration of the results obtained allow us to make certain conclusions which are of importance for the present investigation. The first thing to draw attention to itself is the fact that the shape of the true evaporation curves (curves of Group a) while remaining qualitatively without change during evaporation of molybdenum from granites and diorites, differ appreciably from Group b curves. The most important characteristic of the evaporation curves is the existence of a more or less extended "plateau" *; this corresponds to the first minutes of arc burning and is masked on the curves of the second group by the influence of effects connected with the excitation of the spectra of atoms falling into the plasma of the arc (Curves c).

The existence of such a "plateau" on the evaporation curves points to a hold-up in evaporation of molybdenum from the mineral during the course of the first few tens of seconds of arc burning. This hold-up, is presumably connected with reduction with time of Mo from a more volatile state (in which it is originally found) to a less volatile metallic state. Intense evaporation of the molybdenum from the mineral starts again later – from the second minute of the exposure. The experimental results obtained thus confirm the assumptions put forward earlier [5], on the passing of molybdenum and elements like it into the flame of the arc. Consideration

---

* In certain cases, after the arc had been burning for 30 seconds, there was observed even a small decrease in the total intensity of Mo evaporation, the extent of which remained constant subsequently for 1-2 minutes.

of the curves shown in Fig. 5, also convince one that the displacement of the calibration curves for determination of Mo in granites and diorites, is really only bound up with differences in the conditions for evaporating the element from these minerals, and, in particular, with the fact that in diorites, the secondary intensive passage of molybdenum into the plasma of the arc starts almost a whole minute earlier than in granites.*

As regards excitation conditions for the atoms of molybdenum (Curves c), they remain practically unchanged for all the minerals studied. In order to check up on the correctness of the last conclusion, measurements were made of arc temperature during all the exposure time while the Mo is evaporating from granites and diorites. Temperatures were determined by Ornstein's method [6]; this method is applicable to sources in which the spectra are excited thermally. In this case, the logarithm of the ratio of the intensity of the spectral lines in the spectrum of the element (I_{ik}) to a value which is proportional to the probability of the respective transition (P_{ik}), should be a linear function of the ratio E_i/T, where E_i is the energy of the higher level of the transition of the spectral line considered, while T is the absolute temperature. Accordingly, by measuring the relative intensities of several lines of the same element with known values of the probability of the transition and energy of the upper levels, in the spectrum of the test source, and representing graphically the relation between the logarithms of the ratios $\frac{I_{ik}}{P_{ik}}$ $\frac{E_i}{T}$, it is possible, under conditions of thermal equilibrium to determine arc temperature from the value of the slope of the straight line thus constructed. This method has been widely used for measuring the relative probabilities of line transitions for a number of elements, and for investigating processes which occur in various types of sources used for spectrum excitation.

TABLE 2

Energies of the Upper Levels and the Values of the Probability of Transition for Certain Lines of Fe I

λ	Designation of series	E of the upper level in cm^{-1}	P_{ik}
3067,25	$a^5F_4 - x^5D_3^0$	39 970	362
2735,48	$a^5F_3 - w^5D_2^0$	44 184	760
2584,54	$a^5F_5 - x^5D_6^0$	45 608	890

In the course of the present work, when using Ornstein's method for determining arc temperature, use was made of results relating to the values of transition probability (P_{ik}) and to the energy levels of certain iron lines taken from [7]; they are given in Table 2.

On Fig. 6 are given, as an example, results for measurement of arc temperature during evaporation of Mo from diorite. The energies of the upper level of the respective Fe lines in cm^{-1} are plotted along the abscissa, while the value $^1/_{0.625} \log \frac{I}{P}$ is plotted along the ordinate. Near each of the eight straight lines, each of which corresponds to a different exposure time, varying from 30 seconds to 4.5 minutes, is placed the calculated temperature corresponding to it. It is evident that the changes in temperature with time follow the same path as

---

* It was also shown experimentally that evaporation of Mo from minerals richer than diorite in calcium and magnesium (which were introduced artificially into the minerals) starts even sooner. Thus, for a content of 20% of Mg in the mineral, secondary passage of Mo into the plasma of a D. C. arc starts off 60 seconds after the arc starts burning.

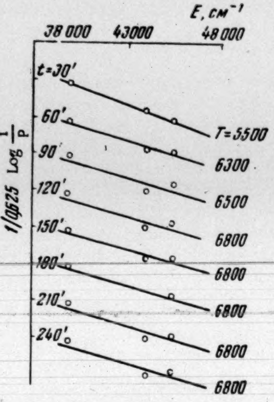


Figure 6. Curves for determination of arc temperature by Ornstein's method.

that taken by Curve c in Fig. 5. In both cases there is observed a gradual increase in the function in the course of the first two minutes of exposure; it then remains constant. Exactly similar results were obtained for granitoids. The absolute values of the temperatures measured also coincided within the accuracy usual for such experiments.

A Method for Calculating the Effect of Bulk Composition of a Mineral on the Results of Quantitative Determination of Molybdenum in Granitoids

In the previous section it was shown that the displacement of the calibration curves for determination of molybdenum during its evaporation from granites and diorites can be related to the earlier passage of part of the molybdenum of diorites into the arc plasma, and to the burning out of these atoms of the element in conditions which are less favorable than those under which atoms of molybdenum evaporating from granites are excited. In a subsequent series of experiments an attempt was made to find out the change, in those particular components of the minerals that distinguish the composition of a diorite from granites, with which one can connect the fact established experimentally, that there is an increase in the number of molybdenum atoms passing into the plasma of the arc in the period preceding its intensive evaporation from

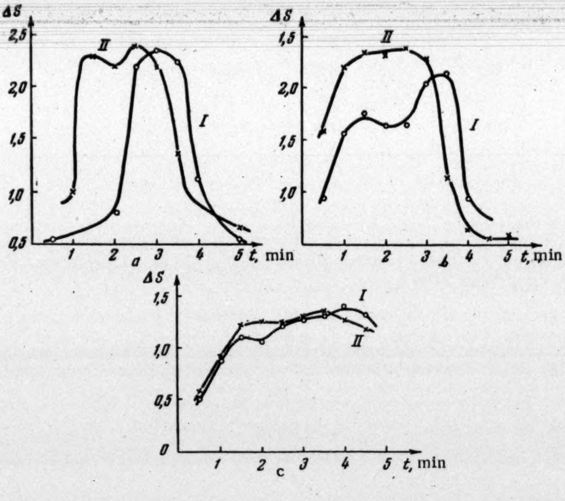


Figure 7. Evaporation curves of Ca a, Mg b, and Si c from granite I and diorite II.

minerals with a granite composition. These particular elements are, as shown by analysis, Ca and Mg. In contrast to the other components of the mineral, the evaporation curves of which remain practically unchanged in granitoids and diorite, most of the Ca and Mg in diorite evaporates considerably earlier than in granitoids, and presumably take with them some of the molybdenum from the mineral. That this is a correct assumption can be ascertained by consideration of the evaporation curves given in Fig. 7, on which the group of Curves a and b relate to Ca and Mg, while Curves c characterize the behavior of Si. One arrives at the same conclusion directly by comparing the shape of calibration curves for the determination of Mo in granite, diorite, and synthetically prepared samples similar in composition to granite, into which were successively introduced the oxides of Ca, Mg, Fe, and Al in such amounts that they brought the contents of these elements in the samples up to values characteristic for diorite. On Fig. 8 are shown a group of such calibration curves. It is evident from a consideration of such curves that addition of the respective amounts of the oxides of Fe and Al to the granite does not alter the position of the calibration curve, while addition of the oxides of Mg and Ca displace it sharply towards diorite. At the same time, the position of the calibration curve for diorite remains practically unchanged on addition to this mineral of SiO_2 and alkalis in amounts which bring up the amounts of SiO_2 and the alkali in the mineral to values which are characteristic of granite.

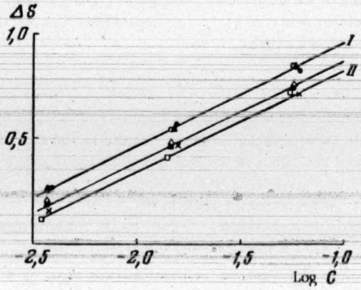


Figure 8. Calibration curves for determination of Mo from granite I, diorite II and granite with synthetic additions of the oxides of Fe (Δ), Al (O), Ca (Δ) and Mg (!!) and diorite with additions of SiO_2 (□).

It turned out that the relation between the position of the calibration curve for determination of molybdenum in a rock and its Ca and Mg content is not limited to a purely qualitative one; it is fairly regular. For the group of rocks under consideration, the value of the displacement of the graph in comparison with its position for granite, to a first approximation proved to be a linear function of the contents of Ca and Mg respectively in the rock.

What has been said is illustrated by the graph given in Fig. 9. The value of the displacement of the calibration curve, expressed in intensity units is plotted along the ordinate, while the relative content of Ca and Mg in the rock is plotted along the abscissa. In the special case, for a rock with an approximately constant ratio of Ca to Mg, as one would expect, there is a simpler ratio, which is represented graphically in Fig. 10. This permits one, during spectrographic determination of Mo in rocks of the group under discussion, to suggest a simple method for calculating the effect of the bulk composition of a test sample and, in this way, improve analytical accuracy considerably. On a plate on which has been registered the spectra of molybdenum in rocks, in addition to the spectra of standard samples prepared on a granite basis of a definite chemical composition, is registered yet another spectrum, that of a standard sample of diorite composition with a known ratio of Ca and Mg to Si. Subsequently, the blackenings of the analytical lines of Mg, Ca, and Si are measured; then, using the relation between the displacement of the calibration curve with respect to granite, and the value of the relative content of Ca and Mg in the rock, the position of the calibration curve for determination of the Mo content in each of the rocks is made more accurate. In our experiments, we used the following lines of the principal elements for this purpose: Ca – 2997.31 A, Mg – 2776.69 A and Si – 2438.78 A.

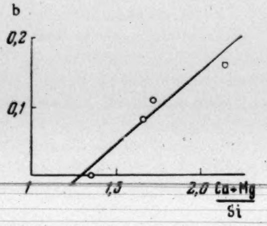


Figure 9. Relation between the value of the displacement of the calibration curve for determination of Mo in rocks b, and the relative content of Ca and Mg in them.

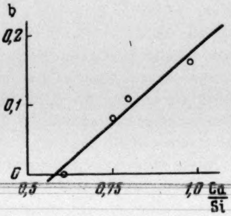


Figure 10. Ditto as for Fig. 9, but for a rock with an approximately constant ratio of Ca to Mg.

TABLE 3

Results of Spectrographic Determination of Mo in Granitoids and Diorite, Before and After Taking into Account the Effect of the Bulk Composition of the Rock

Mo content of rock in %		
Spectrographic determination		Results obtained by chemical analysis
Before correction	After correction	
$1.2 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$
$5 \cdot 10^{-4}$	$6.3 \cdot 10^{-4}$	$7.3 \cdot 10^{-4}$
$1.6 \cdot 10^{-2}$	$1.7 \cdot 10^{-2}$	$1.78 \cdot 10^{-2}$
$2 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$	$3 \cdot 10^{-4}$
$1.2 \cdot 10^{-4}$	$2.8 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$

The efficiency of the method suggested for calculating the effect of the principal elements on the results of spectrographic determination of Mo in granites, granodiorites, and diorites is illustrated by the figures given in Table 3.

SUMMARY

1. It has been shown that calibration curves for determination of molybdenum in granitoids and diorite are parallel, but are uniformly displaced with respect to one another.

2. A method has been suggested for studying the processes of evaporation and excitation of elements in the source, based on the use of marked atoms. By means of this method it is possible to study evaporation of the element and its excitation in the source separately.

3. A systematic study has been made of the conditions for excitation and evaporation of molybdenum from granitoids and diorite, which enables one to understand the reasons for the displacement of the calibration curves for determination of this element in different rocks.

4. It has been established that within the limits of the group of rocks considered, the magnitude of the displacement of the calibration curve for determining molybdenum, as compared with its position for granite, is, to a first approximation, proportional to the content of Ca and Mg in the rock.

5. On the basis of the experimental results obtained, a method has been suggested for calculating the effect of the bulk composition of rocks on the results of spectrographic determination of molybdenum in them, and examples of its practical application given.

LITERATURE CITED

[1] P. Kuroda and E. Sandell, Geochim. et Cosmochim. Acta 6, 35 (1954).

[2] V. V. Nedler, Factory Lab. 7, 795 (1938).

[3] E. E. Vainshtein, T. F. Borovik-Romanova and V. V. Korolev, J. Anal. Chem. 10, 158 (1955) (T. p. 147).*

[4] E. E. Vainshtein and V. V. Korolev, J. Anal. Chem. (In the press).

[5] A. K. Rusanov, "Spectrographic Analysis of Ores and Minerals" (State Geol. Press, 1948), p. 51.

[6] L. Ornstein, Brinkman and Hengtum, Physica 5, 145 (1938).

[7] N. N. Sobolev, J. Expt.-Theor. Phys. 13, 131, 137 (1943).

Received February 15, 1956

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

THE EFFECT OF IRON ON THE COLORIMETRIC DETERMINATION OF CERIUM

R. K. Korabelnik

Moscow Steel Institute

Small amounts of cerium are usually determined colorimetrically [1]. In the methods used, the intensity of the colors of solutions of quadrivalent cerium is measured [2]. Less specific, but more sensitive methods are those based on the use of its oxidizing properties, in particular, those involving the use of redox indicators [3].

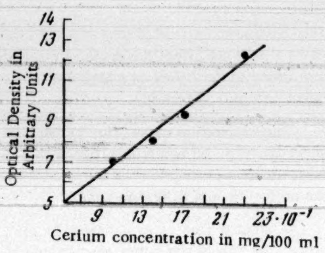


Figure 1

We set ourselves the problem of varying experimental conditions in order to increase the specificity of the methods involving the use of redox indicators, and settled on ferroin as a redox indicator having a higher normal oxidizing potential than other redox indicators recommended in the literature: tolidine (+0.87 V), phenylanthranilic acid (+1.08 V), diphenylamine (+0.76 V). Ferroin is a complex compound of o-phenanthrolin with divalent iron and has a red color. With strong oxidizing agents ferroin gives a complex with trivalent iron which has a blue color. The reaction is reversible. The normal oxidation potential of this redox indicator in 1 N H_2SO_4 is 1.14 V. The normal oxidation potential Ce^{4+}/Ce^{3+} is 1.45 V.

With pure cerium salts we got a calibration curve (Fig. 1) which obeys the Lambert-Beer law within the concentration limits 0.7-2.3 mg in 100 ml solution. The high acidity of the solution is necessary in order to prevent the solutions from getting turbid as the result of hydrolysis.

Experimental Procedure. Into a 100 ml flask was measured out from a buret a known volume of cerium sulfate solution; excess 0.025 M ferroin (10 drops) was then added. The solution was diluted with distilled water to 100 ml and its color measured.

Best results were obtained when working with a yellow filter. The light filter used has a maximum transmission in the blue part of the spectrum (the oxidized form of ferroin is blue in color).

The work was carried out on a Ts. ZA photocolorimeter and on a Pulfrich photometer. Determinations were made in duplicate. Further increases in the amount of cerium led to the appearance of a greenish color (instead of the blue which is characteristic of the oxidized form of ferroin). The appearance of the green color may be attributed to insufficient ferroin at high cerium concentrations. In such cases, the yellow color of the unreduced quadrivalent cerium is superimposed on the blue color of the oxidized form of ferroin, and thereby yields a green color.

The amount of indicator that should be added depends on the amount of cerium presumed to be in solution. Since the reaction of quadrivalent cerium with ferroin is not specific, it follows that it must be carried out in the absence of other oxidizing agents, whose normal oxidation potential is higher than +1.14 V (the potential of ferroin); thus, MnO_4^- and $Cr_2O_7^{2-}$ interfere with the determination of cerium.

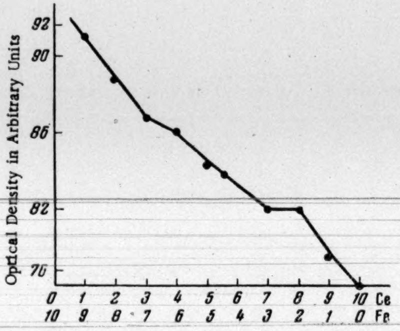


Figure 2

One would expect that trivalent iron with a potential of +0.77 V will not affect the shape of the calibration curve during cerium determination. All the same, it was established in the course of a series of tests that iron does affect the reaction which takes place between quadrivalent cerium and ferroin.

The calibration curve (Fig. 2) obtained in the presence of iron is a broken line with a straight line section. The shape of the curve does not depend on the amount of ferroin added.

In order to find an explanation for the straight line part of the curve, we carried out a series of experiments whose results are given on the diagram of state - property (by Kurnakov's method [4-6]). The saddle on the diagram indicates the possibility of the formation of a new compound (Fig. 3).

In order to find the composition of the compound thus formed we studied the light absorption of the same mixtures of cerium and iron salts in the absence of ferroin. In this case again there is a saddle on the diagram. Thus, at certain ratios of cerium and iron (3 moles of $Ce(SO_4)_2$ and 1 mole of $NH_4Fe(SO_4)_2 \cdot 12H_2O$) formation of a compound of the type of a double salt or complex compound is observed.

It should be pointed out that the Italian scientists Ferrari, Cavalca and Nardello [7], obtained and isolated a complex compound formed between trivalent cerium and divalent iron of the following composition: $K_5Ce[Fe(NO_2)_6]_2$.

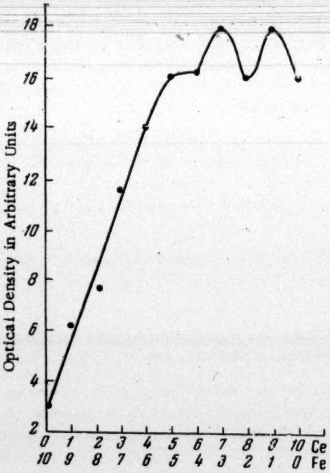


Figure 3

Formation of a complex compound of quadrivalent cerium with trivalent iron is even more probable.

We attempted to isolate the compound formed from more concentrated solutions of cerium and iron, taken in the same ratios. Under the polarizing microscope, transparent crystals of a yellow color in the form of small barrels of cubic syngony were visible. These crystals were very unstable and deliquesced in air. On evaporating a drop on glass, the crystals broke up. For other quantitative ratios of the salts of cerium and iron, individual crystals characteristic for cerium salts, and poorly developed crystals of iron salts, were observed.

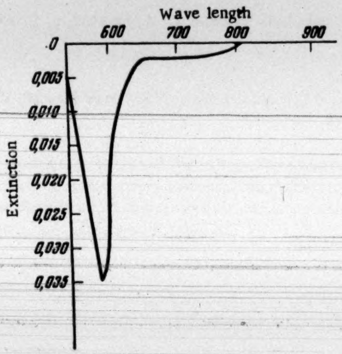


Figure 4

In view of the difficulty of isolating such unstable compounds, we used a spectrophotometric method [7] for confirmation of their formation in solution. Spectrophotometric curves of the following solutions were taken: a) solutions of cerium salts free from iron; b) solutions of salts containing cerium and iron in the ratio of 9 moles to 1 mole; c) solutions of salts of cerium and iron taken in equal concentrations; d) solutions of cerium and iron salts in concentrations corresponding to the area on the photocolorimetric curve.

In the first three cases, the curves proved to be parallel to one another; in the last instance there was observed a sharp deviation from the normal shape of the spectrophotometric curve at 550-650 mμ.

In Fig. 4 is given the differential curve which shows the difference in the optical densities of solutions of quadrivalent cerium and trivalent iron in the ratio ~3 moles to 1 mole. As is evident from the curve, maximum deviation is observed at 580 mμ.

Thus, at the ratios indicated, there is formed a compound between cerium and iron, which may be one of the reasons which leads to distortion of the photocolorimetric curves.

SUMMARY

1. It has been shown that it is possible to determine cerium colorimetrically in solutions of its salts by means of ferroin.

2. It has been shown that the presence of iron in solution, at certain concentrations, distorts the results obtained.

3. Microcrystalloscopic and spectrophotometric studies have confirmed the formation of complex compounds at ratios of cerium to iron of 3 : 1.

LITERATURE CITED

[1] J. Plank, Z. anal. Chem. 116, 312 (1939).

[2] D. I. Ryabchikov and Z. G. Strelkova, J. Anal. Chem. 3, 4, 126 (1948).

[3] D. I. Ryabchikov, E. A. Terenteva and Yu. Sklyarenko, Trans. Commission on Analytical Chemistry, Vol. III (VI), p. 63 (1951).

[4] I. V. Tananaev, Bull. Platinum Division, 1948, No. 21, p. 203.

[5] I. V. Tananaev, J. Anal. Chem. 3, 1, 31 (1948).

[6] I. V. Tananaev, J. Anal. Chem. 3, 5, 276 (1948).

[7] Adolfo Ferrari, Luigi Cavalca and Mario Nardello, C. A. for 1952, p. 12753.

Received May 26, 1955

ACCURATE VOLUMETRIC DETERMINATION OF GAMMA AMOUNTS OF MERCURY

V. I. Kuznetsov and E. V. Mitrofanova

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow

During a study of the theoretical aspects of the extraction of elements, we became aware of the absence of any published methods for the accurate determination of very small (gamma) amounts of mercury. This induced us to develop a new method which is described below; this method gives accurate results for the determination of both macro and micro amounts of mercury.

A number of methods have been described in the literature for the determination of mercury; these however, do not give accurate results for the determination of very small amounts of mercury. These include a method which was published recently for the spectrophotometric determination of mercury on the basis of the absorption of a mercury cyanate complex in the ultraviolet [1]; colorimetric methods based on the use of dithizone [2-4], diphenylcarbazide [5], 4,4'-bis-(dimethylamino) thiobenzophenone [6], the method of Shtock and coworkers, the inaccuracy of whose method has already been emphasized in the literature [7], etc.

TABLE 1
Determination of Mercuric Chloride by Titration with Potassium Iodide Using "Starch-Iodide" Indicator (volume 5-7 ml)

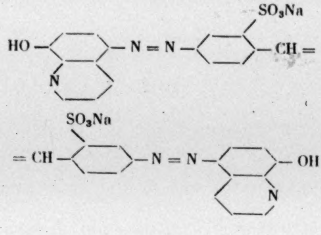
Amount of Hg taken in γ	Amount of Hg found in γ
0,5	1,2; 1,8;
1,0	3,1; 2,1; 3,5
7,0	8,2; 9,1; 8,0
10,0	11,2; 12,3

One comes up against determination of small amounts of mercury in sanitary-hygiene analyses. In such analyses the very inaccurate, semi-quantitative method of H. G. Polezhaev is used almost exclusively; this method is based on colorimetric measurements of the color of a precipitate of Cu_2I_2, colored with mercuric iodide [8]. The method recommended for microdetermination of mercury, involving titration of mercury with iodides using "starch-iodide" indicator [9], proved insufficiently accurate in experiments which we carried out. The end point is not clear cut and titration has poor reproducibility.

The results which we got on titrating gamma amounts of mercury with solutions of ethylenediaminetetraacetate (Trilon B, Complexone III, Versene) using Eriochrome Black T as indicator [10] were unsatisfactory.

After trying out a number of methods, we came to the conclusion that titration of mercuric salts with iodides is the most suitable method for accurate determination of micro amounts of mercury. As a result of the very small value of the ionization constant of the final ion HgI_4^{2-} [$K_{HgI_4^{2-}} = 5 \cdot 10^{-31}$] [11], which differs by several times from the ionization constant of $HgCl_2$ [$K_{HgCl_2} = 1.6 \cdot 10^{-13}$] [12], titration with iodides is suitable for determination of mercury present as the chloride.

Having studied a number of the indicators described in the literature and found them of little use, we tested out the suitability of a number of new (not yet described in the literature) organic reagents which give color reactions with mercury. The best one found was a new reagent; the disodium salt of stilbene-4,4'-bis [(azo-5)-8-hydroxyquinoline] 3,3'-sulfonic acid which has the following structure:



For brevity we shall call this reagent stilboxine.

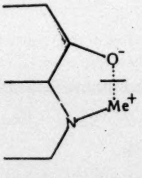
Stilboxine, whose synthesis is described at the end of the present article, is a dark brown material which dissolves in water to give a brown colored solution. On strong acidification of aqueous solutions a dark brown precipitate of the free acid of the reagent is precipitated; on addition of alkali the color changes to violet. Stilboxine is stable for an unlimited time both in the solid state and in (non-alkaline) aqueous solutions.

Theory of the Color Reaction

Stilboxine gives color reactions with a number of elements which form complex compounds with the 8-hydroxyquinoline group. The colors which develop during these color reactions, are connected with the occurrence in the cyclic salts formed of so-called intra-molecular dissociation, and, accordingly, in accordance with the hypothesis advanced previously [13], the shade of the colors of the solutions of these complex salts lies between the colors of solutions of the reagent in acid media (brownish) and in alkali media (violet); the nearer to the color of the alkaline solutions of the reagent, the greater the development of intra-molecular dissociation in the complexes.

Participation of the ionic state of the reagent in the color of the complex is clear from a comparison of the light absorption curves of solutions of the reagent in an acid medium, where it does not have the ionic state of the phenolic hydrogen atom; in alkaline media, where this ionic state is strongly manifested; and of a mercury complex, in which, according to the theory of intra-molecular dissociation of cyclic salts, the ionic state of the phenolic hydrogen atom (Fig. 1) is also manifested to some extent.

It is easy to see that for occurrence of color reactions, it is essential that the bond between the atom of the element and the hydrogen atom of the 8-hydroxyquinoline residue should be ionic in character;



Accordingly, it is readily seen that only those elements which, by forming an ionic bond with a hydrogen atom, can be held in a complex by a non-ionized bond with the nitrogen atom can give color reactions with stilboxine. Such elements will be those tending to form stable ammines in aqueous media, i.e., Pd, Cu, Hg, Ag, Co, Ni, Cd, Zn. These elements, in weakly acid media, at a pH which is suitable for each element, give color reactions with stilboxine — violet colors of varying shades. The shades alter with pH in accordance with general rules [13].

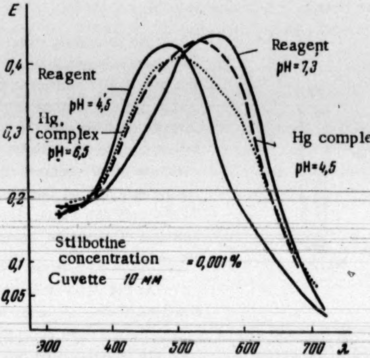


Figure 1. Light absorption of solutions of the reagent stilboxine and its Hg complex.

At pH 4.5, violet colors of varying shades are given by Hg, Co, Cd, Ag, Ni, Zn. Cu gives a rose color. In addition, stilboxine can give colored solid phase reactions with a number of elements [14], leading to the appearance of rose colors. Other elements, which do not form ammines, can still react with stilboxine to give complexes; the color of solutions of such complexes however, is identical with that of solutions of the reagent itself (in acid media).

Determination of the End Point During Titration

Many complexometric methods do not give the highest possible accuracy because of incorrect use of the indicator. During titrations of the type

$$Hg^{2+} + 4I^{-} \rightarrow HgI_4^{2-}$$

and similar ones, the end point is determined by means of an indicator in the form of a reagent (HR) which gives a colored reaction product with the cation of the element which has been bound into a complex

$$Hg^{2+} + 2HR \rightleftarrows HgR_2 + 2H^{+}$$

(HR and HgR_2 have different colors)

It is evident that for an indicator to be suitable for a particular complexometric titration, the concentration of mercury ions, found in equilibrium with the indicator compound formed — $[Hg]_{HgR_2}$ — should be somewhat higher than the concentration of mercury ions — $[Hg]_{HgI_4^{2-}}$, in equilibrium with the complex HgI_4^{2-}, for equal concentrations of iodides and indicator. It is also obvious that in order to carry out titration with highest possible accuracy, when dealing with micro amounts of mercury in very dilute solutions, the values of $[Hg]_{HgR_2}$ and $[Hg]_{HgI_4^{2-}}$ should, in general, be very small. But, however small $[Hg]_{HgR_2}$ and $[Hg]_{HgI_4^{2-}}$ are, and however favorable the ratio of these values, titration will never be accurate enough, if the end point is taken as that point at which there is complete change in indicator color.

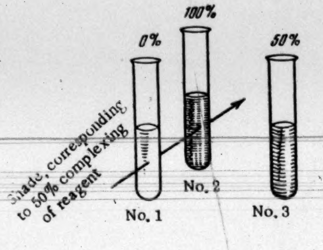


Figure 2. Production of color shade corresponding to the reagent complexed to the extent of 50%.

An absolutely exact determination of this point is, in general, impossible. It is not easy to determine even the practically complete achievement of this titration end point, since it is normally impossible to observe the difference between changes of the indicator into one of the forms, e.g. to 98 or 99.5%. Only during titration of large amounts of the element is it possible to get acceptable results on finishing the titration – after "complete" change of the indicator color. During titration of very small amounts of elements, completely unsatisfactory results are obtained.

At the same time, the overwhelming majority of complexometric methods described in the literature recommend titration up to the point of complete color change. Such recommendations are given for the numerous titrations of many elements with ethylenediaminetetraacetates using Eriochrome Black as indicator, and for many others [9].

Titration accuracy increases appreciably if one stops titrating before complete change of indicator into some other one of its forms. The most convenient point for stopping titration is that point at which 50% of the indicator present (reagent) is bound into a complex with the metal. Stopping titration at this point is most suitable both from the point of view of ionic equilibrium and from optical considerations, since, in mixtures of equal amounts of the differently colored states of the indicator, insignificant changes in shade can be more readily observed than at any other ratios.

These considerations, which are obviously of general significance, are essential if one is to be sure of the highest possible accuracy of determination during titration in very dilute solutions.

In order to determine the shade corresponding to the half-change of the indicator into another form, i.e., the shade at which one should stop titrating, the following simple technique can be used.

Into two identical test tubes are introduced equal amounts of indicator (reagent); they are then diluted with a solution of the necessary pH, i.e., the pH at which titration will be carried out; into one of the test tubes (No. 2) is then introduced just the right amount of a solution of the test element, such that the reagent will be completely converted into the complex compound. That this state has been reached can be checked by observing the absence of any change in color on addition of some more of the solution containing the test element. In this test tube therefore, the reagent is in the completely complexed form, i.e., it is 100% saturated with test element. We shall call the shade thus obtained the "100% saturation" shade.

No element is added to the other test tube (No. 1). After the volumes of the solutions in the two tubes have been made equal, they are observed together, as shown in Fig. 2; we then get a "50% saturated" shade, i.e. the shade which a reagent solution would have when only half of it has been complexed with test element.

This will be the shade at which one should stop titration. For convenience this "indicator" can be prepared in one test tube. To do this, one should introduce into a third test tube (No. 3) just the same amount of reagent as was contained in the first and second tubes taken together, and introduce enough of the element so that the color in test tube No. 3 becomes identical to that of the color produced by holding the other two test tubes together.

During standardization of the complexing agent solution, and when titrations are being carried out on test material, titration is carried on, up to the point where there is exact agreement between the color of test solution and that of the standard color produced as described above.

During preparation of this standard with the "50% saturation" color, difficulties can sometime arise during preparation of a solution corresponding to "100% saturation". On addition to reagent solutions of excess of the element, formation of precipitate sometimes occurs, which in certain cases is even accompanied by a colored solid phase reaction [14], leading to spoiling of the color. In such cases, one should add that amount of element to the test tube to be used for the "100% saturation" color, which does not lead to formation of precipitates. By doing this, it is possible that only a 90% shade will be obtained; this will naturally lead to a final shade of only 45%. This latter fact is not essential. Titration can quite satisfactorily be stopped when only a 40-45% shade has been reached.

Selectivity of the Method and Attainable Experimental Accuracy

Determination of mercury is impossible in the presence of heavy metals which form complexes with stilboxine. Since the most successful methods of separating mercury, which are based on distillation of mercury [15, 16], lead to its removal from other elements, the insufficiently high selectivity of the method does not introduce any essential complications.

TABLE 2

Determination of Mercury in Pure Solutions

Titration conditions				Mercury in the form of $HgCl_2$		
Volume of solution in ml	Amount of buffer solution in ml	Amount of Stilboxine containing Hg, in ml	Normality KI	Taken in γ	Found in γ	Error in %
4—5	0,5	0,40	0,00006	0,50	0,49	—2,0
4—5		0,40	0,00006	1,00	0,99	—1,0
4—5	0,5	0,40	0,00006	2,00	2,02	+1,0
4—5	0,5	0,40	0,00006	5,00	5,02	+0,5
4—5	0,5	0,40	0,00006	10,00	10,00	±0
5	0,5	0,40	0,0003	20,0	20,2	+1,0
5	0,5	0,40	0,0003	40,0	40,3	+0,7
5	0,5	0,40	0,0003	50,0	49,7	—0,5
5	0,5	0,40	0,0003	80,0	79,5	—0,6
5	0,5	0,40	0,0003	100,0	99,3	—0,7
6—10	0,7	1,00	0,006	200,0	198,8	—0,6
6—10	0,7	1,00	0,006	500,0	499,5	—0,1
6—10	0,7	1,00	0,006	1000	993	—0,7

The accuracy which it is possible to achieve for determination of different amounts of mercury, when the method described below is used, is shown by the examples given in Table 2.

Determination of Mercury

This method is suitable for determination of Hg^{II} in pure solutions of the nitrate, acetate, and chloride. Mercuric bromide is determined with lesser accuracy.

Solutions Required

1. An aqueous solution of the reagent – stilboxine

5 mg of the dry preparation is made into a suspension in ~ 5 ml of water; the suspension is heated and a saturated solution of $NaHCO_3$ added while stirring vigorously, until the precipitate dissolves; care should be taken not to add excess $NaHCO_3$. The solution is diluted to 80 ml with water, and a 0.5-1% solution of CH_3COOH added dropwise until the color changes from a brown-violet color, if that is the color formed, to a yellow-brown; the solution is finally diluted further to 100 ml.

2. Aqueous $HgCl_2$ solution

a) a solution, containing 1.00 mg of Hg in 1 ml. 135.4 mg of $HgCl_2$ are dissolved in water and the volume made up to 100 ml;

b) a solution containing 100 γ Hg in 1 ml is prepared by diluting Solution a ten times.

3. A solution of the reagent stilboxine, containing mercury

To 100 ml of an aqueous solution of stilboxine is added 1.87 ml of the solution of $HgCl_2$, containing 100 γ of Hg in 1 ml.

4. Potassium iodide solutions

a) 0.006 N (0.1%); used for the determination of 100-1,000 γ Hg

b) 0.003 N (0.005%); used for the determination of 10-100 γ Hg^{II}

c) 0.00006 N (0.001%); used for the determination of 0.5-10 γ Hg^{II}

5. Acetate buffer solution — pH 4.5

2.66 g of $CH_3COONa \cdot 3H_2O$ are dissolved in a small amount of water; 1.05 ml of acetic acid (98%) is added, and the volume made up to 200 ml with water.

Procedure for Carrying Out Titration

If the amount of mercury to be determined is known, though only approximately, then the appropriate potassium iodide solution should be chosen; otherwise, one starts off with the most dilute potassium iodide solution.

0.5-2 ml of test solution, which should be neutral or not more than 0.001 N with respect to HNO_3 or CH_3COOH is placed in one of two similar test tubes, while into the other test tube an equal or slightly greater volume of water is added. Next, into both test tubes are introduced exactly equal amounts of stilboxine solution containing mercury — 0.4-1 ml — depending on the volume of the solution. 0.5-1 ml of buffer mixture is finally added to each. The test solution is titrated from a micro-buret with potassium iodide solution of chosen concentration, until the color coincides with that of the solution in the second test tube (the standard color), the volumes of the solutions being equalled by addition of water. The potassium iodide solutions are standardized in the same way with a mercury salt solution.

Synthesis of the Reagent "Stilboxine"

Synthesis consists in diazotization of diaminostilbenedisulfonic acid, and combining the bis-diazo compound prepared with 8-hydroxyquinoline.

1. Diazotization of Diaminostilbenedisulfonic Acid

2.65 g of 100% (2.70 g of the 92.5% product) diaminostilbenedisulfonic acid is dissolved in 40 ml of water by addition of 1.25 g of anhydrous sodium carbonate; 0.95 g of $NaNO_2$ dissolved in 5 ml of water is added, and the solution filtered free of extraneous matter. The filtrate is poured in a fine stream, with good mixing into a mixture of 5 ml HCl (sp. gr. 1.16-1.17) and 5 ml of water containing a few lumps of ice. After 30 minutes, the reaction mixture, which shows a clear-cut reaction for the azo acid, is filtered off through a funnel under suction. The light precipitate of the bis-diazo compound is washed with a small amount of water, transferred into a beaker, and made into a suspension in 15-20 ml water.

2. Combination of the Diazo Compound with 8-Hydroxyquinoline

1.90 g of 8-hydroxyquinoline is dissolved on slight warming in 20 ml ethyl alcohol. After cooling this solution to room temperature, the suspension of the diazo compound is added rapidly with vigorous stirring to it. A solution containing a red-orange colored precipitate is obtained immediately; this color changes to dark brown after some time. After continuous stirring for an hour, 5 ml of a filtered solution of saturated sodium carbonate is added. The color changes to violet. Stirring and mixing is continued for a further 1-4 hours, and then slowly, dropwise, is added 25 ml of acetic acid, followed finally by 5 ml of HCl (sp. gr. 1.16). The mixture is gradually heated on a boiling water bath, filtered while hot, and the product washed with 50 ml hot water.

To purify the product it is suspended in 500 ml of warm water, dissolved by addition of ammonia, and the violet solution filtered off from insoluble residue; it is then precipitated by slow addition, first of acetic acid, and then of hydrochloric acid. The product is filtered off, washed with water, and dried in air. A dark brown product is obtained; yield ~ 9.3 g.

SUMMARY

1. Solutions of the reagent stilboxine – stilbene-4,4'-bis [(azo-5) -8-hydroxyquinoline]-3,3'-disulfonic acid – have a brown-yellow color at a pH of ~ 4.5; this color changes to violet on addition of $Hg(NO_3)_2$ or $HgCl_2$.

2. By titrating solutions of pure $HgCl_2$ with potassium iodide in the presence of stilboxine at a pH of ~ 4.5 (acetate buffer), it is possible to determine 0.5-1000 γ Hg in a volume of 4-10 ml with an accuracy of up to 0.5-1%.

3. High accuracy is possible when titration is carried on to the point where a red-violet color is obtained which corresponds to complexing of the reagent by mercury to the extent of 50%. Titration is carried out with the use of a reference color.

4. The synthesis of the reagent stilboxine is described.

LITERATURE CITED

[1] G. E. Markobe and D. F. Boltz, Anal. Chem. 26, 447 (1954).

[2] Sugihara Takeshi, C. A. 46, 10257 (1952).

[3] H. Irving, G. Andrew and E. J. Risdon, J. Chem. Soc. 1949, 541.

[4] Marie Houskova, from Abs. J. Chem. 1954, 43090 (No. 19).

[5] Miranda Ottino, Bull. chim. farm. 88, 245 (1949).

[6] B. Gehaut and J. Goldenson, Anal. Chem. 22, 498 (1950).

[7] P. H. Schulitz, Arch. Pharm. 286, 506 (1953); from Abs. J. Chem. 1954, 39967.

[8] N. G. Polezhaev, Hygiene of Labor and Safety Technique 6, 86 (1936).

[9] N. M. Korenman, "Quantitative Micro-Chemical Analysis" (State Chem. Press, 1949), p. 233; N. V. Koshkin, Factory Lab. 8, 677 (1939).

[10] W. Biedermann and G. Schwarzenbach, C. A. 42, 3694 (1948).

[11] F. P. Treadwell and V. G. Hall, "Quantitative Analysis" (State Chem. Press, 1946), p. 42.

[12] K. B. Yatsimirsky, Progr. Chem. 22, 410 (1953).

[13] V. I. Kuznetsov, J. Gen. Chem. 20, 807 (1950) (T. p. 845).*

[14] V. I. Kuznetsov, Progr. Chem. 18, 75 (1949).

[15] A. A. Saukov and N. Kh. Aidinyan, Factory Lab. 10, 147 (1941); D. N. Finkelshtein and I. B. Petropavlovskaya, Factory Lab. 20, 155 (1954).

[16] I. M. Korenman, "Quantitative Micro-Chemical Analysis" (State Chem. Press, 1949), p. 271.

Received May 25, 1955

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

COPRECIPITATION OF CADMIUM WITH ANTIPYRINE TETRABROMOMERCURIATE

I. M. Korenman and A. A. Tumanov

Scientific Research Institute for Chemistry at the Gorky State Universtiy

Antipyrine is being used on an ever increasing scale in analytical chemistry. Ryabchikov and Terenteva [1] prepared a number of complex salts formed between antipyrine and the rare earths. Antipyrine can give compounds with

$$[Fe(CN)_6]^{3-},\ [Fe(CN)_5NH_3]^{2-}\ \text{and}\ [Co(CH)_6]^{3-} \qquad [2]$$

Antipyrine forms complex compounds with a number of divalent cations. Gusev [3], found that antipyrine-bromide reagent in acid media gives a complex compound with cadmium, which permits cadmium to be determined qualitatively and quantitatively in alloys. Formation of complex compounds of divalent metals is possible in neutral media. In such cases, according to Kumov [4], the composition of the salts obtained correspond to the formula

$$[Me(C_{11}H_{12}ON_2)_2]X_2,$$

where

$$Me - Zn^{2+};\ Cd^{2+};\ X - Cl^-;\ Br^-;\ I^-;\ CNS^-.$$

A nephelometric method has been developed for determination of mercury as antipyrine tetraiodomercuriate [5].

We showed experimentally that divalent mercury forms a sparingly soluble compound.

$$(C_{11}H_{12}ON_2)_2 \cdot H_2[HgBr_4] \cdot 2C_{11}H_{12}ON_2.$$

with antipyrine and bromine. This compound has been used by us for the separation of small amounts of cadmium by coprecipitation.

Since ionic radii of cadmium and mercury are near in size (Hg^{2+} 1.12 A; Cd^{2+} 1.03A) one should expect isomorphous substitution of mercury by cadmium. The choice of mercury as the macro component is a convenient one, since, when necessary, it can readily be separated from cadmium by calcining.

For rapid and convenient determination of small amounts of coprecipitated cadmium, we used the radioisotope Cd^{115}. The initial specific activity of the working solution of cadmium nitrate was 50,000 impulses/minute/mg of cadmium. Solutions of varying (lower) specific activities were prepared from this stock solution as the occasion demanded.

It was established in preliminary experiments that the precipitate with the antipyrine-bromide reagent is only formed at comparatively high cadmium concentrations (for the preparation of the reagent see below). At cadmium concentrations of less than 70 γ/ml, no precipitate is formed. Accordingly, during the study of coprecipitation of cadmium, the concentrations used were always considerably less than 70 γ/ml.

Experiments were carried out as follows. To 1 ml of a $Hg(NO_3)_2$ solution containing micro amounts of cadmium was added 1 ml of antipyrine-bromide reagent. After one hour the precipitate was separated from the mother liquor and washed with a mixture of diethyl ether and ethyl alcohol (7: 1); it was then dried to constant weight at 100° and the cadmium content determined radiometrically. In addition, the activities of the wash liquor and mother liquor were determined respectively.

In order to find out what the effect of the HNO_3 concentration of the reagent is on cadmium coprecipitation, we dissolved 5 g of antipyrine and 10 g of potassium bromide in 85 ml of HNO_3 of various concentrations. The solution contained 2 or 5 mg of mercury and 41 γ of cadmium.

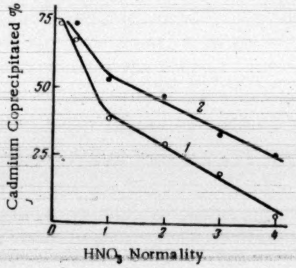


Figure 1. Coprecipitation of cadmium as a function of nitric acid concentration: 1) during precipitation of 2 mg of mercury; 2) during precipitation of 5 mg mercury.

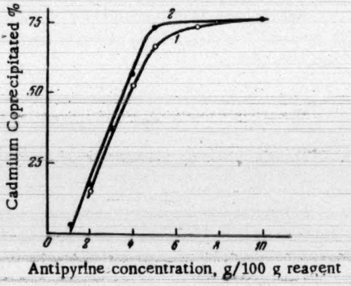


Figure 2. Coprecipitation of cadmium as a function of antipyrine concentration: 1) during precipitation of 2 mg of mercury; 2) during precipitation of 5 mg mercury

Figure 1 shows that with increasing HNO_3 concentration in the antipyrine reagent, the amount of coprecipitated cadmium decreases, particularly when the amount of mercury is small; this is presumably the result of the solubility of the antipyrine tetrabromomercuriate. Observations show that if the mercury is to be precipitated so that the amount of cadmium coprecipitated is a maximum, then precipitation should be carried out from 0.2 N HNO_3. To 1 ml of the test solution, therefore, 0.05 ml of 4 N HNO_3 was added before precipitation.

Next we studied the effect of antipyrine concentration, the concentrations of nitric acid and potassium bromide being kept constant; followed by the effect of potassium bromide concentration when nitric acid and antipyrine concentrations respectively were kept constant. The reagents had the following composition: a) 1-10 g antipyrine and 10 g potassium bromide in 100 g aqueous solution (Fig. 2); b) 1-30 g potassium bromide and 10 g antipyrine in 100 g solution (Fig. 3).

Experiment showed that with increasing antipyrine concentration, the amount of coprecipitated cadmium increases. Coprecipitation of cadmium increases appreciably up to a concentration of 7 g of antipyrine in 100 g reagent, and then changes very little up to 10 g antipyrine.

Increasing potassium bromide concentration also leads to an increase in the amount of cadmium coprecipitated with antipyrine tetrabromomercuriate (Fig. 3). A reagent containing 20 g of potassium bromide in 100 g solution, gives a maximum cadmium coprecipitation, probably as the result of an increase in the amount of precipitate.

The results obtained (Figs. 2 and 3), enable one to select the optimum concentrations of antipyrine and potassium bromide at which cadmium can be coprecipitated in solutions of fairly low acidity. In all our subsequent experiments we used a solution of 10 g antipyrine and 20 g of potassium bromide in 70 ml of water. 1 ml of test solution was always acidified with 0.05 ml of 4 N HNO_3, and 1 ml of precipitant was used. During a study of the effect of the concentrations of the macro and micro components on the extent of cadmium coprecipitation, under the optimum conditions, the cadmium concentrations amounted to 41, 33, 25, and 16 γ/ml (Fig. 4).

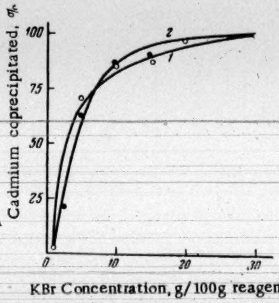


Figure 3. Coprecipitation of cadmium as a function of the potassium bromide concentration: 1) during precipitation of 2 mg mercury; 2) during precipitation of 5 mg mercury.

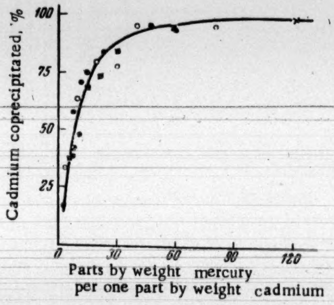


Figure 4. Coprecipitation of cadmium as a function of the cadmium and mercury concentrations: − 41 γ cadmium; ⊙ − 33 γ cadmium; Δ − 25 γ cadmium; ⊗ − 16 γ cadmium.

It is interesting to note that the percentage coprecipitation of cadmium is a function of the ratio of the amounts of mercury and cadmium. Independently of the absolute amounts of cadmium, all the results lie on one curve (Fig. 4), which is described by the empirical equation

$$\text{Log}\ \frac{[Hg^{2+}]}{[Cd^{2+}]} = 1{,}73 \cdot 10^{-2} q,$$

where $\underline{q}$ is the percentage cadmium coprecipitated; $[Cd^{2+}]$ and $[Hg^{2+}]$ are the initial concentrations of the components in γ/ml.

The calculated percentage coprecipitation of cadmium practically coincides with the experimental values (Table 1).

When divalent mercury is precipitated with a reagent prepared according to Gusev's method,* the percentage cadmium coprecipitated is less than in cases where the precipitant used is a more concentrated solution of the antipyrine-bromide reagent.

The micro component is trapped by the precipitate of the macro component as a result of the formation of isomorphous mixtures, adsorption, etc. In order to find out the nature of the coprecipitation in this case, we carried out the following series of tests.

---

* 5 g antipyrine and 10 g potassium bromide in 85 ml 0.5 N HNO_3.

TABLE 1

Amount of Coprecipitated Cadmium

Concentrations of components in γ/ml		$[Hg^{2+}]/[Cd^{2+}]$	Amount of Cd coprecipitated (q) in %	
Hg	Cd		As calculated from the formula	As determined experimentally
500	36	14	66	67
500	28	18	72	78
500	20,5	24	80	84

Trapping of Cadmium by Antipyrine Tetrabromomercuriate Formed Beforehand

During the study of trapping of cadmium by antipyrine tetrabromomercuriate formed beforehand, a definite amount of the mercury was precipitated in one case from an active solution by addition of the antipyrine-bromide reagent, while in the other case, the same amount of crystalline antipyrine tetrabromomercuriate prepared beforehand was introduced into a solution containing the same amount of cadmium and thoroughly mixed. After 20 minutes, the precipitates were removed and the amount of cadmium coprecipitated determined in each case.

In our test, to 1 ml of solution acidified with 0.05 ml of 4 N HNO_3 and containing 41 γ cadmium was added 15 or 23 mg of fine crystalline antipyrine tetrabromomercuriate. In the precipitate which was separated only a little cadmium (~ 3%) was found; this indicates the probability of isomorphous separation of cadmium.

The Effect of Agar-Agar on Cadmium Coprecipitation

If cadmium is attracted into the precipitate to form an isomorphous mixture with antipyrine tetrabromomercuriate, then coprecipitation should be independent of the presence of protective colloids introduced into the solution prior to precipitation of the mercury.

Into a solution acidified with 0.05 ml of 4 N HNO_3 was added 40 γ cadmium and 2 mg mercury and various amounts of a freshly prepared aqueous solution of agar-agar of known concentration.

From Fig. 3 it is clear that in the absence of protective colloids coprecipitation of cadmium under these conditions approximates to 100%. Agar-agar has no observable effect on cadmium coprecipitation. On increasing agar-agar concentration from 0.001 to 0.08%, the percentage coprecipitation remained practically unchanged. It should also be noted that some univalent cations, which do not give a precipitate with the antipyrine-bromide reagent, have no effect on the amount of cadmium coprecipitated.

Effect of Temperature on Cadmium Coprecipitation

With the aim of getting purer precipitates, precipitation is often carried out at elevated temperatures in order to decrease the adsorption of other (foreign) ions.

A series of tests was carried out to establish the effect of temperature on cadmium coprecipitation. In the first series, 1 ml of the mixture to be precipitated contained 41 γ cadmium and 0.5 mg of mercury, while the other contained 50 γ cadmium and 2 mg mercury. In both cases, the solution was acidified with 0.05 ml of 4 N HNO_3 and precipitated with 1 ml reagent. After precipitation, the solutions plus precipitates were kept for one hour at the respective test temperature; the precipitates were then removed from mother liquors and washed. In some experiments the amount of coprecipitated cadmium was determined immediately, while in others, the precipitates were dried to constant weight, weighed, and their cadmium content determined. The amount of cadmium coprecipitated with 1 mg of precipitate was then calculated (Table 2).

These results show that the amount of cadmium coprecipitated, related to one part by weight of precipitate, remains practically constant. The drop in the absolute amount of cadmium coprecipitated with increasing temperature can be explained by the decrease in weight of the precipitate as a result of increasing solubility.

TABLE 2

Effect of Temperature on Coprecipitation of Cadmium

Temperature in °C	41γ Cd^{2+} and 0,5 mg Hg^{2+}		50γ Cd^{2+} and 2 mg Hg^{2+}			
	Cd coprecipitated		Cd coprecipitated		Weight of precipitate in mg	γ Cd/mg precipitate
	γ	%	γ	%		
0	21	51	—	—	—	—
16	17	42	—	—	—	—
18	—	—	47	94	20,4	2,3
30	17	42	40	80	16,6	2,4
40	15	36	39	78	16,9	2,3
50	14	34	38	76	15,9	2,4

Effect of the Time for Which the Precipitate is in Contact with Mother Liquor

Coprecipitation of cadmium does not depend on the time for which the antipyrine tetrabromomercuriate is in contact with the mother liquor. Even after 190 hours contact between precipitate and mother liquor, no observable change in the amount of cadmium coprecipitated could be detected.

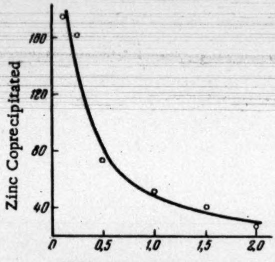


Figure 5. Effect of nitric acid concentration on coprecipitation of zinc.

All the results considered above permit one to conclude that cadmium is trapped in the antipyrine tetrabromomercuriate precipitate mainly as the result of isomorphous substitution of mercury by cadmium.

As pointed out already, during precipitation of divalent mercury with antipyrine-bromide reagent, 100% of the cadmium present is coprecipitated under certain conditions. It has also been pointed out that zinc does not have any essential effect on the amount of cadmium coprecipitated, and is coprecipitated with cadmium or mercury. We thought it might be possible to find conditions for precipitating mercury, such that cadmium would be precipitated in maximum amounts, while zinc would be precipitated in minimum amounts, and thus develop a method for separating cadmium from zinc salts. With this aim in view therefore we studied the coprecipitation of zinc * with antipyrine tetrabromomercuriate, in relation to nitric acid concentration and zinc concentration, and also studied the coprecipitation of zinc during repeated precipitation of mercury in the presence of small amounts of cadmium.

Effect of Nitric Acid on the Coprecipitation of Zinc with Antipyrine Tetrabromomercuriate

The 2 ml of mixture to be precipitated always contained 5 mg mercury and 10 mg zinc, while the amount of nitric acid was varied. Mercury and zinc were in the form of their nitrates. The mixture was stirred and 1 ml of precipitant (10 g antipyrine and 20 g potassium bromide in 70 ml water) added. After one hour the precipitate was removed and the zinc in it determined radiometrically.

---

* Determination of small amounts of coprecipitated zinc was carried out radiometrically by means of the radioactive isotope Zn^{65}.

It is clear from Fig. 5 that on increasing the nitric acid concentration in the mixture to be precipitated, the amount of zinc coprecipitated decreases.

Effect of Zinc Concentration on Its Coprecipitation

The experimental conditions were kept the same as before. In these cases,however, 10 to 50 mg of zinc were added to tests containing constant amounts of mercury (5 mg Hg^{2+}) and 1 N HNO_3 (Table 3).

TABLE 3

Effect of Zinc Concentration on Its Coprecipitation.

Zn^{2+} content in mg	Zn coprecipitated	
	in γ	in %
10	55, 55, 46	0,52
20	98, 80, 75	0,44
30	177, 162, 167	0,56
40	182, 177, 191	0,46

It is clear from Table 3 that on increasing the zinc concentration, the absolute amount of zinc coprecipitated increases, though the percentage coprecipitated decreases. Small amounts of cadmium (20 and 40 γ) do not affect coprecipitation of zinc with antipyrine tetrabromomercuriate.

When mercury is precipitated from a mixture with zinc salts containing small amounts of cadmium under conditions such that coprecipitation of zinc is a minimum, then appreciable amounts of cadmium are coprecipitated, and it cannot be removed completely from the precipitate by washing. For a fuller separation of cadmium from zinc salt solutions, successive precipitation of equal amounts of divalent mercury was used. From 2 ml of the original volume, 1 N with respect to HNO_3, and containing 50 mg zinc and 25 γ cadmium, we carried out four precipitations using 5 mg of mercury each time. The precipitate was washed twice with a mixture of diethyl ether and ethyl alcohol and then analyzed for cadmium. Table 4 contains the results of four parallel determinations.

It is clear from Table 4 that of the 25 γ of cadmium contained in the 50 mg Zn, we managed to separate over 20 γ. For the chemical detection of traces of cadmium, we proceeded as follows. The precipitate of antipyrine tetrabromomercuriate obtained by successive precipitation of 20 mg of mercury was calcined in a porcelain crucible at 700°. After cooling, the inner surface of the crucible was treated with 0.2 ml of 2 N HNO_3, and cadmium detected by the reaction with cadion in an alkaline medium [6]. By this method we succeeded in separating and detecting as little as 5 γ of cadmium in 50 mg of zinc. Similar experiments were carried out with the aim of separating traces of cadmium from copper salts. When divalent mercury is introduced into a

TABLE 4

Separation of Cadmium from Zinc Salts

Successive precipitation of mercury	Tests					
	1		2		3	
	Cadmium coprecipitated					
	in γ	in %	in γ	in %	in γ	in %
1	16,4	65,8	16,7	66,8	16,8	67,2
2	3,4	13,6	3,5	14,0	3,3	13,2
3	0,8	2,3	0,7	2,8	0,9	3,6
4	0,2	0,8	0,3	1,2	0,2	0,8
Total cadmium separated	20,8	82,4	21,2	84,8	21,2	84,8

solution of a copper salt containing traces of cadmium, and the mercury is precipitated with antipyrine-bromide reagent, then cadmium is coprecipitated with the precipitate formed. Copper does not affect coprecipitation of cadmium.

The experiments were carried out as follows: 1 ml of 0.1 or 0.4 M cupric nitrate, which contained 40 γ cadmium and 2 mg of mercury, was acidified with 0.05 ml of 4 N HNO_3 and precipitation effected by addition of 1 ml reagent. After one hour the precipitate was separated by centrifugation, and washed with reagent till the wash liquor gave a negative test for copper. The precipitate was dissolved in hydrochloric acid (1 : 1), and part of the solution analyzed for copper and another part for cadmium.

It was established in this way that copper is not coprecipitated with antipyrine tetrabromomercuriate, while at the same time, in both cases, upwards of 50% cadmium was detected.

SUMMARY

1. Coprecipitation of zinc and cadmium occurs when divalent mercury is precipitated with antipyrine-bromide reagent.

2. The respective effects of the concentration of nitric acid, antipyrine, potassium bromide, and that of the macro and micro components, as well as the effect of temperature, the length of time for which the precipitant is allowed to act, and other factors on coprecipitation of cadmium have been studied. Coprecipitation of cadmium with antipyrine tetrabromomercuriate proceeds primarily by isomorphous substitution of mercury by cadmium.

3. The effect of nitric acid concentration and zinc concentration, respectively, on coprecipitation of zinc with antipyrine tetrabromomercuriate has been studied.

4. It has been established that precipitation of mercury in the form of antipyrine tetrabromomercuriate can be used for separation of small amounts of cadmium from solutions of zinc and copper salts respectively.

LITERATURE CITED

[1] D. I. Ryabchikov and E. A. Terenteva, Proc. Acad. Sci. USSR 51, 287 (1946).

[2] S. I. Gusev and R. G. Beilis, J. Org. Chem. 21, 1971 (1951).

[3] S. I. Gusev, J. Anal. Chem. 4, 175 (1949).

[4] V. I. Kumov, J. Org. Chem. 21, 1965 (1951).

[5] S. I. Gusev, J. Anal. Chem. 5, 375 (1950).

[6] L. P. Adamovich and E. Yu. Novik, Sci. Trans. Kharkov State University 37, 29 (1951).

Received July 10, 1955

BLANK
PAGE

AN ABSORPTION-PRECIPITATION CHROMATOGRAPHIC TECHNIQUE FOR THE SEPARATION OF NICKEL AND COBALT BY MEANS OF DIMETHYLGLYOXIME

A. M. Gurevich

Institute of Physical Chemistry, Acad. Sci. USSR

The similarity of the physicochemical properties of nickel and cobalt leads to considerable difficulties when attempts are made to separate them. A vast amount of data has been published on the various methods of solving this problem (see e.g. [1-3]). The hypochorite method used in industry for purifying cobalt [1, 3] gives a product which contains appreciable amounts of nickel as an impurity. Dimethylglyoxime * which with nickel forms a precipitate which is not soluble in water [5], is often used for getting a more pure preparation. Nevertheless, in view of the fact that Co also reacts with H_2Dm, it is necessary to take sufficient excess of dimethylglyoxime to react both with the cobalt and with nickel [6]; when this is done, Co is practically completely complexed by the H_2Dm. Moreover, according to F. Feigl [7], nickel dimethylglyoxime is appreciably soluble in the solution of cobalt dimethylglyoxime.

A complete separation of Ni and Co can be achieved by Feigl and Kapulitzas' [8] method, which is recommended by the authors both for the purification of cobalt salts from nickel [9], and for the determination of small amounts of Ni in the presence of large amounts of Co. All the same, this method is not ideal since it involves the use of potassium cyanide. A good but rather complicated method for freeing Co from Ni by using cobalt pentamine, has been used for determining the atomic weight of Co [1].

Recently, a large number of articles have been published in which Tsvet's chromatographic method [10] has been used for the separation of Ni and Co. Schwab and Jokers [11], who were the first to use this method for the separation of inorganic materials, separated Ni from Co by chromatographic separation of the cations from ammoniacal solutions on aluminum oxide. Erlenmeyer and Dahn [12], who used 8-hydroxyquinoline for separating cations, found, in particular, that it is possible to separate Ni from Co in this way (see also [13]). Burriel-Marti and Perez [14], have described the use of a H_2Dm column for determination of small amounts of Ni.

Al-Mahdi and Wilson [15] separated Ni and Co in the form of their compounds with sodium diethyldithiocarbamate, by chromatographing them from an organic solvent on aluminum oxide. The limit of identification for Ni is 2 γ in the presence of 10 γ Co; and the limit of identification for Co is 0.738 γ in the presence of 18 γ Ni. Among other methods for the chromatographic separation of Ni and Co, mention should be made of their separation as the glycine complexes [16]; those in which they were separated on cellulose columns [17]; and on ion-exchange resins [18]; and also quite a large number on their separation by means of paper chromatography [19, 20].

Not one of the chromatographic methods enumerated for separating Ni and Co can be regarded as convenient for the purpose of freeing cobalt salts from Ni.

---

* Dimethylglyoxime will henceforth be designated by H_2Dm [4].

Purification of Cobalt Salts from Small Amounts of Nickel Impurities

Using the principle of precipitation chromatography of T. B. Gapon and E. N. Gapon [21-23], in conjunction with adsorption chromatography, we developed a simple method for the chromatographic separation of Ni and Co, which is suitable for purifying Co from Ni. The method suggested is based on the use of columns containing a mixture of dimethylglyoxime and an adsorbent. In contrast to the columns of H_2Dm used by Burriel-Marti and Perez [14], for detecting Ni in the presence of Co, Fe^{2+} and Pd, we mix H_2Dm (for the purpose of purifying Co from Ni) with activated charcoal (usually in the ratio 1: 10) and under this layer we place pure charcoal for adsorbing any dimethylglyoxime washed out of the top layer (C. f. [28]). In this way H_2Dm and cobalt dimethylglyoxime are prevented from getting into the filtrate. At the same time the cobalt salt which has saturated the column (since the amount of Co is in excess of the amount which is equivalent to the H_2Dm content of the column) passes into the filtrate, free from nickel, and also free from any substances not contained in it before purification.

On feeding the solution into the column, Ni reacts with H_2Dm sooner than Co to form the upper zone, and continuously displaces cobalt from its compound with H_2Dm forming the lower zone, while both zones extend right up to the point where the Co passes into the filtrate; the onset of this point is very rapid, in the absence of impurities which exhibit a buffer action (we ignore zone mixing as a result of desorption-adsorption processes at this stage). If it is assumed that Co^{2+} reacts with H_2Dm in solution to form the compound $Co(HDm)_2$ [24], then replacement of cobalt by nickel from its compound with H_2Dm can be represented by the following equation:

$$\mathrm{Ni}^{2+} + \mathrm{Co(HDm)_2} \rightleftarrows \mathrm{Ni(HDm)_2} + \mathrm{Co}^{2+}. \tag{1}$$

A necessary condition for this reaction to proceed to the left is

$$K_1 = \frac{K_{\mathrm{diss.\ Co(HDm)_2}}}{L_{\mathrm{Ni(HDm)_2}}} > 1. \tag{2}$$

It follows $K_{\mathrm{diss\ Co(HDm)_2}} > L_{\mathrm{Ni(HDm)_2}}$ ($L_{\mathrm{Ni(HDm)_2}} = 2.2 \cdot 10^{-25}$ [25]). The "multistage character" of this process in a fairly linear chromatographic column, and the adsorption capacity of the charcoal ensure, at least for low Ni contents (of the order 2-3%) in the original cobalt salts, absence of Ni in analytically determinable amounts, even in the first portions of filtrate, despite their relatively low pH. In such a case, addition of sodium acetate to the original solution is completely optional. Ni cannot be detected in the purified solution by any known methods of chemical analysis, nor by a method described below.

In our experiments we used glass tubes with diameter of 6-12 mm, stopped at one end with a plug of cotton wool. We used birch charcoal with grain size of 0.2 mm cross-section. The lower layer of the column consisted of pure charcoal, the amount of which was 50-100% of its amount in the upper layer, which itself was a mixture of charcoal with H_2Dm powder in the ratio 10 : 1. The solution was fed through the column under gravity. It is worth while, having fed the column with solution, to stop the experiment for a certain time, and soak the column with water or, alternatively, soak the column a few hours before the run. This operation ensures a higher column efficiency.

For a molar ratio [Ni]: [Co] of the order of 0.02-0.03, the efficiency coefficient of H_2Dm was ~ 0.2, i.e. before Ni gets into the filtrate, ~20% of the H_2Dm in the column is used up in complexing the Ni. It should be noted that the efficiency coefficient of H_2Dm depends to a large extent on a number of factors, in particular, on experimental technique; it drops in the presence of oxidizing agents, including the NO_3^- ion. A large amount of oxidizing agent, e.g. $(NH_4)_2S_2O_8$, makes separation impossible.

Qualitative Determination of Ni and Co in Their Mixtures

For the detection of Ni and Co salts we used a column of a mixture of chromatographic aluminum oxide and dimethylglyoxime in a ratio of 10 : 1. Burriel-Marti and Perez [14] used, for this purpose, either pure H_2Dm

or its mixture with $CaCO_3$ or $MgCO_3$. The use of Al_2O_3 as a carrier in a column has, to our mind, a number of advantages. Aluminum oxide of chromatographic quality, has a good filtering capacity, thanks to which the technique of filling it into columns is considerably simplified. Al_2O_3 adsorbs the complex compounds of cobalt with H_2Dm, forming uniform, clear-cut zones, which allows small amounts of Co to be determined as well as Ni, even for a large excess of Ni. By strongly holding the finely dispersed precipitate of $Ni(HDm)_2$ on its surface, aluminum oxide ensures that one gets an uniform and relatively dense Ni zone, while on carriers of the type of $CaCO_3$, $MgCO_3$, and $BaSO_4$, as Burriel-Marti and Perez also pointed out, a large number of rose bands of $Ni(HDm)_2$ are formed. Finally, chromatographic aluminum oxide acts as a pH regulator, mopping up acid formed during the reactions, thanks to which, during the use of neutral and weakly acid solutions, additions of such compounds as sodium acetate or ammonia are not necessary for the determination of either Ni or Co.

The mixture of Al_2O_3 and H_2Dm is introduced into a tube closed at one end with a plug of cotton wool; it is then tamped down by tapping and is wetted with water. On such a column a solution of Ni^{2+} and Co^{2+} forms a chromatogram consisting of two zones: a rose-red zone of nickel and a yellow cobalt zone. On washing the chromatogram with water, the Co zone rapidly extends and moves downwards, as a result of which the separation becomes very clear.

It should be pointed out here that in actual fact, Co gives, apparently, no less than two zones, the colors of which differ sharply from the color of the solution formed by cobalt on mixing with H_2Dm.

Preliminary wetting of the column with water is of primary importance. On passing a solution containing Co into a dry column, reaction proceeds in the same way as when a solution of Co^{2+} is mixed with H_2Dm; the brown compound of Co with H_2Dm formed in the column pores, passes into the filtrate which is not held back by the column. We should also like to note, that in contrast to processes occurring in dimethylglyoxime columns, in solution nickel does not displace Co^{2+} from its compound with H_2Dm, obtained by mixing a solution of H_2Dm with a small excess of cobalt [24]. All this points to a complex relation between the structure of the compounds formed between Co and H_2Dm, and the conditions under which they are formed.

The sensitivity of the detection of Ni in the presence of cobalt depends primarily on the following constant factors. It is obvious, above all, that the lower the Ni concentration in the test solution for an equal concentration of cobalt, the lesser the extent to which the equilibrium (1) will be shifted to the side of $Ni(HDm)_2$ formation. Accordingly, at a relatively low concentration of Ni, there is formed a mixed zone of Ni and Co, in which the concentration of Ni is less than in solution. This, in turn, leads to a decrease in the intensity of the color of the nickel zone in the washed chromatogram. Secondly, the smaller the volume of solution taken for analysis, all other conditions being the same, the narrower the nickel zone and consequently the more difficult it is to detect.

Oxidizing agents, just as in the case of charcoal-dimethylglyoxime columns, leads to deterioration in the separation. Such reducing agents as Na_2SO_4 also have a negative effect on the sensitivity of detection of Ni. In both cases, particularly when excess strong oxidizing agent is present, the shape of the cobalt zone changes essentially. In the presence of $(NH_4)_2S_2O_8$, e.g., cobalt, instead of a yellow zone, formed two brown zones which differ somewhat from one another with respect to intensity and shade.

For analysis of small volumes of solution, we used a tube 3.5 mm in diameter, into which had been introduced a dry mixture of aluminum oxide (chromatographic quality) with dimethylglyoxime in the ratio 1:10; this was tamped down by tapping, wetted with water, and then tamped down again as recommended by Komlev and Tsimbalista [26]. After this the upper layer of the column (1-2 mm) was removed; in this layer the uniformity of the distribution of H_2Dm and Al_2O_3 had been destroyed (in the presence of appreciable amounts of Ni in the test solution, the last two operations are optional). Into the column prepared in this way was introduced 0.1 ml of test solution (the Co^{2+} concentration in it usually did not exceed 0.5 N) and then immediately after the solution had soaked in, the column was washed with 0.1-0.2 ml of water. For very low concentrations of Ni^{2+} and a large excess of Co^{2+}, one should make a blank test with a solution of Co salt purified from Ni. In this way it was possible to detect as little as 0.4 γ Ni at a dilution of 1:250,000 and a 3700-fold excess of cobalt. Under such conditions Ni gives a characteristic rose-red zone on top of a light yellow Co zone, which is not observed in tests with a purified Co solution. In individual cases we succeeded in determining Ni in an amount less than 0.4 γ with a 4000 fold excess of Co (here, as in other cases of precipitation of crystalline precipitates, the region where one gets unreliable reactions is relatively large [7]).

Burriel-Marti and Perez [14], state that they succeeded in detecting 0.2 γ Ni in the presence of 10,000 times its amount of Co on a H_2Dm column. It should be borne in mind however that ammonia was added to the solution before analysis, as a result of which a large part of the Co was precipitated, as the authors themselves note, so that the ratio of [Co]: [Ni] decreased considerably. According to our observations, the sensitivity of Ni determination in Co salts on solumns containing a mixture of Al_2O_3 and H_2Dm in a ratio of 10 : 1, is not less than the sensitivity of determination of Ni on H_2Dm columns.

By means of Al_2O_3 and H_2Dm columns it is possible to detect relatively small amounts of Co^{2+} at the same time as Ni^{2+}. Thus, on a column 3.5 mm in diameter it is possible to detect 2.9 γ Co at a dilution of 1: 34,500 and 500 times its amount of nickel. In such cases Co gives a narrow yellow band in the washed chromatogram; the color tends to darken on long standing.

Other cations can be separated on columns of the type described. In particular, by using a charcoal-dimethylglyoxime column, Co^{2+} can be separated not only from Ni^{2+}, but also from Cu^{2+}, which is found in the upper zone. Using a column of a mixture of Al_2O_3 + H_2Dm, we got a chromatogram for Ni^{2+}, Fe^{2+}, and Co^{2+}, cations which formed a mixed zone on a column made up of aluminum oxide alone [11, 27].

The method described here, which is based on the use as carrier of a material which adsorbs the compounds formed between the cations to be separated and a reagent, mixed with the carrier, or adsorbed by the carrier, may be useful both for analysis and for separation of cations with the object of purifying them, and for studying physicochemical properties of soluble compounds formed between cations and organic materials.

SUMMARY

1. An adsorption-precipitation chromatographic method is described for purifying cobalt from nickel; columns consisting of a mixture of activated charcoal- dimethylglyoxime placed over a layer of pure charcoal were used.

2. A method has been worked out for detecting traces of Ni^{2+} in Co^{2+} salts, and of small amounts of Co^{2+} in the presence of excess Ni^{2+}; the columns in these cases consisted of a mixture of aluminum oxide and dimethylglyoxime.

LITERATURE CITED

[1] F. M. Perelman, A. Ya. Zvorykin, and N. V. Gudman, "Cobalt" (Acad. Sci. USSR, Press,1949).

[2] I. W. Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry (Longmans, Green and Co., London, New York, Toronto, 1935), 14, 1440.

[3] R. S. Young, Cobalt (New York, 1948).

[4] A. K. Babko, J. Anal. Chem. 3, 284 (1948).

[5] L. A. Chugaev, "Research in the Field of Complex Compounds" (1906), 59.

[6] V. M. Peshkova, Sci. Proc. Moscow State University 78, 3 (1945).

[7] F. Feigl, Spot Analysis (Gen. Sci. Tech. Press, 1937), 255; F. Feigl "Spot Tests" (1954), 1, 141.

[8] F. Feigl and H. J. Kapulitzas, Mikrochemie, Emich-Festschrift, 8, 128 (1930).

[9] F. Feigl and H. J. Kapulitzas, Z. anal. Chem. 82, 417 (1930).

[10] M. S. Tsvet, Trans. Warsaw Natural Sciences Soc. Biol. Div. 14, 20 (1903).

[11] G. M. Schwab and K. Jockers, Z. angew. Chem. 50, 546 (1937).

[12] H. Erlenmeyer and H. Dahn, Helv. Chim. Acta 22, 1369 (1939).

[13] F. M. Shemyakin and E. S. Mitselovsky, J. Anal. Chem. 3, 349 (1948).

[14] F. Burriel-Marti and F. P. Perez, Anales real. soc. espan. fis. y. quim. 45B, 749 (1949); Anal. Chim. Acta 3, 468 (1949).

[15] A. K. Al-Mahdi and C. L. Wilson, Mikrochem. ver. Mikrochim. Acta 36-37, 218 (1951); 40, 138 (1952).

[16] H. Flood and A. Smedsaas, Tidsskr. Kjemi, Bergvesen Met., 2, 17 (1942); C. 1942, 2, 1269.

[17] F. H. Burstall, G. R. Davis, R. P. Linstead and R. A. Wells, Nature, 163, 64 (1949); Discussions Faraday Soc., No. 7, 179 (1949).

[18] G. E. Moore and K. A. Kraus, J. Am. Chem. Soc. 74, 843 (1952); E. Blasius and M. Negwer, Naturwissenschaften 39, 257 (1952).

[19] A. Lacourt, et al., Metallurgia 40, 181 (1949); Nature 163, 999 (1949); Mikrochem. ver. Mikrochim. Acta 35, 262 (1950); 36-37, 117 (1951); Bull. soc. chim. 873 (1951); Compt. rend 232, 2426 (1951).

[20] F. H. Burstall, G. R. Davies, R. P. Linstead and R. A. Wells, J. Chem. Soc., 1950, 516; Harasawa Shiro, J. Chem. Soc. Japan, Pure Chem. Sect. 72, 614 (1951); Muraji Shibata and Taku Ucmura, ibid. 72, 541 (1951); B. Milicevic, Bull. soc. chim. Belgrade16, 101 (1951); M. Lederer and F. L. Ward, Anal. Chim. Acta 6, 355 (1952); A. W. Airan, Science and Culture (India), 18, 89 (1952); A. W. Airan and J. Barnabas, ibid 18, 438 (1953); I. S. Binayendra, Australian J. Sci. 15, 133 (1953).

[21] T. B. Gapon and E. N. Gapon, Proc. Acad. Sci. USSR 60, 401 (1948).

[22] E. N. Gapon and I. M. Belenkaya, Colloid J. 14, 323 (1952); 'Research in Chromatography (Acad. Sci. USSR Press,1952) p. 35.

[23] V. V. Rachinsky and T. B. Gapon, 'Chromatography in Biology' (Acad. Sci. USSR Press,1953), pp. 17-21.

[24] A. K. Babko and M. V. Korotun, J. Gen. Chem. 24, 597 (1954) (T. p. 609).*

[25] P. B. Mikhelson, A Study of the Chemico-Analytical Properties of Dimethylglyoxime and Its Compounds with Nickel", Author's Thesis, Kiev, 1954.

[26] A. I. Komlev and L. I. Tsimbalista, J. Anal. Chem. 8, 217 (1953) (T. p. 243).*

[27] K. M. Olshanova and K. V. Chmutov, J. Anal. Chem. 8, 211 (1953) (T. p. 235).*

[28] A. M. Gurvich, T. B. Gapon and M. S. Rabinovich, Chem. Ind., No. 1, 31 (1956).

Received July 3, 1955

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

THE USE OF THIOUREA SOLUTIONS IN VOLUMETRIC ANALYSIS (THIOCARBAMIDOMETRY)

K. B. Yatsimirsky and A. A. Astasheva

Ivanov Chemico-Technological Institute

Thiourea was first used in chemical analysis by L. A. Chugaev who used it as a reagent for osmium [1]. Subsequently, thiourea was used for detecting and determining a number of other elements, both in qualitative and quantitative analysis (colorimetry and gravimetric analysis). Only in one instance was it suggested that thiourea might be used for determining copper volumetrically [2].

Earlier, we carried out a thermochemical study of thiourea complexes [3]. O. S. Fedorova determined the instability constants of the complexes of cadmium, lead, and bismuth respectively with thiourea [4, 5]; a number of complex compounds were isolated in a crystalline state [6]. Knowing the instability constants of thiourea complexes (Table 1), and relying on theoretical principles expounded previously [10], we were able to indicate other ways of using thiourea in volumetric analysis. Direct titration with thiourea is possible in a limited number of cases. Only the thiourea complexes of mercury and, to a certain extent, those of silver and copper * satisfy the condition $pK_n \geqslant 4n + 3$ [11], ($\underline{n}$ is the coordination number). The ions of the metals mentioned, and also those of bismuth, can be masked by thiourea with respect to a large number of reactions.

TABLE 1

Stability of Certain Thiourea Complexes

Composition	pK	4n + 3	Composition	pK	4n + 3
$[Hg(CSN_2H_4)_4]^{2+}$	28,0 [9]	19	$[Bi(CSN_2H_4)_6]^{3+}$	12,0 [5]	27
$[Ag(CSN_2H_4)_3]^{+}$	13,9 [8]	15	$[Cd(CSN_2H_4)_3]^{2+}$	2,9 [4]	15
$[Cu(CSN_2H_4)_4]^{+}$	15,4 [7]	19	$[Pb(CNS_2H_4)_3]^{2+}$	1,8 [4]	15

Thiourea can be used as a complexing agent in a considerably large number of cases with subsequent precipitation of the complexed cations. Methods which we have developed for determining mercury and cadmium are given below as examples.

---

* It is possible that titration can be completed by formation of complexes with a smaller coordination number, and by observation of the condition $pK_n \geqslant 4n + 3$ [11].

Determination of Mercury and Thiourea

Solutions of thiourea of different concentrations (0.025 M; 0.2 M) were used as stock working solutions. Solutions were prepared from chemically pure thiourea after a double recrystallization of the commercial product from alcohol. Such solutions keep for a long time; in neither case were we able to detect any change in the normality of the thiourea solutions over a period of four months.

Standard solutions of mercuric nitrate, 0.025 - 0.1 M, were prepared as usual. These solutions also keep their normality constant over a period of several months. Diphenylcarbazide and β-nitroso-α-naphthol were used as indicators. The latter indicator was suggested by Kulberg and Mustafin for mercurimetric titration [12].

Determinations were carried out as follows. A known volume of the titrant solution of thiourea (10-25 ml) was placed in a conical flask to which was added the indicator (15-20 drops of a saturated alcoholic solution of diphenylcarbazide, or 10 drops of a similar solution of β-nitroso-α-naphthol). The solution was then diluted with water to 100-150 ml and titrated with the solution of $Hg(NO_3)_2$. At the equivalence point, the solution is colored a blue-violet color when diphenylcarbazide is used, or changes its color from a yellow-green to a yellow-orange in the case of β-nitroso-α-naphthol.

The reaction between mercuric ions and thiourea proceeds according to the following equation:

$$Hg^{2+} + 2CSN_2H_4 = Hg(CSN_2H_4)_2^{2+}.$$

Apparently, in the given instance, there are large differences in the step-like instability constants of the complexes $Hg(CSN_2H_4)_2^{2+}$ and $Hg(CSN_2H_4)_3^{2+}$.

TABLE 2

Titration of $Hg(NO_3)_2$ with Thiourea Solutions

	Volume of $CS(NO_3)_2$ solution used for titrating 22 ml of $Hg(NO_3)_2$, in ml	Deviation from mean value	
		in ml	in %
	10,50	+0,02	0,2
	10,50	+0,02	0,2
	10,45	—0,03	0,3
	10,48	0,00	0,0
	10,48	0,00	0,0
	10,45	0,03	0,3
	10,47	—0,01	0,1
	10,50	+0,02	0,2
	10,48	0,00	0,0
	10,50	0,02	0,2
Average	10,48	σ*=0,02	σ*=0,19

---

* σ – mean square deviation

Results are given in Tables 2 and 3 for the statistical treatment of titration of mercury salts with thiourea. The mean square deviation when dephenylcarbazide is used as indicator amounts to 0.2-0.3%, while in the case of β-nitroso-α-naphthol, it is 0.1-0.2%.

It is much more convenient to titrate the thiourea solution with $Hg(NO_3)_2$ solution, rather than the other way round, though the reverse titration is also fully possible. Accordingly, for determination of mercury it is more expedient to add a known excess of thiourea immediately, and then titrate it with $Hg(NO_3)_2$ solution.

The pH of the solution has a very considerable effect on the results of titration. At comparatively high values (pH > 4), mercury salts are broken down by thiourea with formation of HgS precipitate. At high acidity values, diphenylcarbazide cannot be used as an indicator.

When diphenylcarbazide is used as indicator, the optimum pH is 2, while in the case of β-nitroso-α-naphthol wider variations in pH are possible.

Silver, cadmium, lead, zinc, nickel, manganese, magnesium, and ammonium cations, as well as acetate, sulfate, nitrate, and phosphate anions do not interfere with determination of mercury or thiourea (Table 4).

The method developed is accordingly characterized by high accuracy, reasonable specificity, and ease of execution.

TABLE 3

Titration of $Hg(NO_3)_2$ Solution with Thiourea

Working solutions and their concentrations	Number of tests	Indicator	Volume of solution in ml		Mean square deviation	
			$Hg(NO_3)_2$	$CS(NH_2)_2$	in ml	in %
$Hg(NO_3)_2$ 0,05 *M*	9	Diphenylcarbazide	21,05	10,00	0,044	0,2
Thiourea 0,2*M*	10	Ditto	22,00	10,49	0,035	0,3
$Hg(NO_3)_2$ 0,05*M*	9	β-Nitrose-α-naphthol	20,99	10,00	0,021	0,1
Thiourea 0,2*M*	10	Ditto	22,00	10,48	0,020	0,2

TABLE 4

The Effect of Other Materials on the Results of Titration of Thiourea with $Hg(NO_3)_2$ [180,2 mg of $CS(NH_2)_2$ taken]

Amount added in mg (as a solution)		$CS(NH_2)_2$ found in mg and relative error in %			
		Indicator β-nitroso-α-naphthol	Δ %	Indicator – diphenylcarbazide	Δ %
	—	180,4	0,11	180,1	0,06
422	CH_3COOH	179,3	0,52	179,3	0,52
2000	$Pb(NO_3)_2$	180,4	0,11	180,1	0,06
200	$NiSO_4$	180,5	0,16	180,4	0,11
100	NaH_2PO_4	180,9	0,38	180,9	0,38
140	$AgNO_3$	—	—	179,3	0,52
1000	$Cd(NO_3)_2$	181,0	0,44	180,9	0,38
1000	$ZnSO_4$	180,9	0,38	180,9	0,38
1000	$Al_2(SO_4)_3$	180,5	0,16	180,9	0,38
1000	$MnSO_4$	180,5	0,16	180,5	0,16

Determination of Cadmium

On addition to cadmium salts of thiourea and picrate, a crystalline precipitate is formed $[Cd(CSN_2H_4)_4]-(C_6H_3N_3O_7)_2$ [6].

In order to clarify the possibility of using these reactions for volumetric determination of cadmium, it was essential to know the solubility product of the salt formed, and the instability constant of the complex ion. The cadmium complex formed is unstable (compare Table 1); nevertheless the solubility product, as pointed out before [10], has a decisive importance in this case. On the basis of measurements of the solubility of $[Cd(CSN_2H_4)_4^{2+}]-(C_6H_3N_3O_7)_2$ in thiourea solutions containing cadmium, and free from cadmium, respectively,* the solubility product was calculated:

$$[Cd(CSN_2H_4)_4^{2+}]\,[C_6H_3N_3O_7^-]^{2-} = (4{,}8 \pm 0{,}2)\cdot 10^{-11}.$$

---

* Solubility was determined colorimetrically.

During precipitation of the cadmium complex of thiourea, the final concentration of picrate amounts to approximately 10^{-2} M; consequently the $[Cd(CSN_2H_4)_4]^{2+}$ remaining in solution is approximately 5 · 10 M. The lower limit of the method described is the concentration of the cadmium salt and is of the order of $5 \cdot 10^{-4}$ M (precipitation 99.9%).

The method used for determining cadmium consists essentially of the following: after precipitation of the complex salt of cadmium with excess thiourea and picrate, the thiourea content of the filtrate is determined by titration with mercuric nitrate solution using diphenylcarbazide as indicator. Chlorides, bromides, and iodides should be absent.

Analytical Procedure. In a standard 100 ml flask is placed 20 ml of the test solution of cadmium salt (0.01-0.05 M); to this solution is then added 20 ml of 0.25 M thiourea solution, 30-40 ml of a saturated solution of picric acid, and the whole made up to the mark with water. After 15-20 minutes, some of the solution is filtered through a dry filter and an aliquot of the filtrate (20 ml) titrated with 0.025-0.05 M $Hg(NO_3)_2$ solution, using diphenylcarbazide as indicator.

Results for some cadmium determinations are given in Table 5.

TABLE 5

Determination of Cadmium by Precipitation of $[Cd(CSN_2H_4)_4]^{2+}$ with Picrate

Cd taken in mg	Number of determinations	Cd found in mg (mean results)	Deviation of mean result in %	Mean deviation in %
11,08	2	11,07	—0,09	0,14
27,71	2	27,78	+0,25	0,27
44,34	3	44,35	+0,02	0,09
28,20	4	28,19	—0,04	0,25
55,43	5	55,42	—0,02	0,08

σ from 20 experiments is equal to 0.23%
σ — mean square deviation

TABLE 6

Effect of Zinc on the Accuracy of Cadmium Determination

Cd taken in mg	Cd found in mg (mean result)	Ratio (Cd: Zn) in mole	Number of experiments	Deviation in %
55,43	55,59	1 : 100	1	+0,29
55,43	55,25	1 : 200	3	—0,32
46,33	46,22	1 : 300	1	—0,24
55,43	55,23	1 : 500	2	—0,36
46,33	46,50	1 : 1000	1	+0,37

Mercury, bismuth, silver, copper, thallium, and large amounts of lead interfere, since they form similar compounds [6]. The remaining elements do not interfere as long as they are not present in forms which can oxidize thiourea. Determinations can be carried out in the presence of a large excess of zinc ; experimental accuracy is not lowered even in the presence of a 1,000-fold excess of zinc (Table 6).

It should be pointed out however, that in the presence of large amounts of zinc salts, the precipitate is formed more slowly (when the amount of zinc present is ~ 1,000 times that of the cadmium being determined, it is necessary to leave the solution for 22-24 hours for complete precipitation).

SUMMARY

1. A method has been developed for determining mercury by titrating solutions of its salts with thiourea solutions; this method can also be used for determining thiourea.

2. A method has been worked out for determining cadmium, which is based on precipitation of a sparingly soluble complex salt containing thiourea, and titrating excess thiourea with mercuric nitrate.

LITERATURE CITED

[1] L. A. Chugaev, Compt. rend. 167, 225 (1918).

[2] Z. Brada, Anal. chim. Acta 3, 53 (1949).

[3] K. B. Yatsimirsky and A. A. Astasheva, J. Phys. Chem. 27, No. 10, 1539 (1953).

[4] O. S. Fedorova, Collection of Articles on General Chemistry (1953), Vol. 1, p. 206.

[5] O. S. Fedorova, J. Gen. Chem. 24, No. 1, 62 (1954) (T. p. 59).*

[6] K. B. Yatsimirsky and A. A. Astasheva, J. Anal. Chem. 7, 43 (1952) (T. p. 45).*

[7] E. I. Onstott and H. A. Laitinen, J. Am. Chem. Soc. 72, 4724 (1950).

[8] F. G. Pavelka, Z. Electrochem. 30, 180 (1924).

[9] A. T. Pilipenko and G. S. Lisetskaya, Ukrain. Chem. J. 19, 81 (1953).

[10] K. B. Yatsimirsky, J. Anal. Chem. 10, 94 (1955) (T. p. 85).*

[11] K. B. Yatsimirsky, J. Anal. Chem. 7, 206 (1952) (T. p. 235).*

[12] L. M. Kulberg and I. S. Mustafin, Factory Lab. 17, 412 (1951).

Received December 20, 1954

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

EFFECT OF TEMPERATURE ON THE RATE OF ELECTRO-ANALYSIS

V. A. Karnitsky

Rostov Medical Institute

In 1939 - 1941 the author of the present article [1-3], proposed a rapid method of electro-analysis at the boiling point without using mechanical stirrers; it was shown that analysis under these conditions is just as accurate, and can be finished in the same time, as in the usual method when special mechanical stirrers are used. In 1943 the author [4], also established a logarithmic relation between the rate of electro-precipitation of cations and temperature:

$$\log v = a + bt^{\circ} \tag{1}$$

$$\log I = a + b_1 t^{\circ}, \tag{1a}$$

where v is the rate of electro-deposition; t°, temperature in deg.Centigrade; I, current; a and b, empirical constants. Kamyshnikov [5], on the basis of these results, established experimentally that the method of rapid electro-analysis during boiling of the electrolyte without mechanical stirrers is applicable to exact quantitative separation and determination of cadmium and zinc. In their conclusions to the experimental study of the deposition rate of bismuth and cadmium during electrolysis, using a stirrer, Kovalenko and Areva [6], point out that rapid electro-analysis of bismuth and cadmium can be successfully carried out at the boiling point without stirrers also.

In 1950 Gorbachev [7], published an article "The relation between electro-analysis and temperature", in which, on the basis of experimental results and theoretical considerations, a relation was deduced connecting change in the rate of electrolysis, without deposition of solid phase, with temperature; the following equation was given for aqueous solutions:

$$\log I = A - \frac{445}{T}, \tag{2}$$

where I is current strength; T, the absolute temperature; A, a constant. At the same time, in the experiments of Gorbachev and Starostenko [7], on the electro-deposition of metals, results were obtained which when plotted on a graph give curves which do not correspond with the equations given above (1, 1a, and 2). Thus, for the electro-deposition of copper from an aqueous solution of cupric sulfate, the author's experimental results correspond to curves with an obvious maxima for current strength at 60-70°. On increasing temperature further, the current drops sharply. The difference between these curves and those obtained in other cases of electrolysis examined by S. V. Gorbachev, which characterize the electrolysis process with deposition of a solid phase, is also contradicted by other instances (electrolysis without electro-deposition). From these results one could come to the wrong conclusion, viz.that the optimum temperature for rapid electro-deposition of metals is ~ 60-70°, which is also the temperature range which is given in widely used textbooks on electro-analysis [8,9].

The studies described below show however, that the results of S. V. Gorbachev and E. P. Starostenko on electro-deposition cover only special cases which depend on the conditions under which the process is carried out; the statement, made in advanced textbooks on electro-analysis, that a temperature of 60-70° is the optimum, seems to be the result of an incomplete study of the given question. As will be shown, the deposition curves for cations during electrolysis, in the general case, correspond with a good degree of approximation to Equation (1). The optimum temperature for speeding up the process of electro-deposition should be the boiling point of the electrolyte.

Electrolysis of Salts in Aqueous Solutions Containing Various Additives (Electro-deposition)

Experiments on electrolysis of salts were carried out using a platinum disc with surface area 1.32 cm² as cathode, and a platinum spiral as anode. Electro-deposition was carried out at constant potential on the electrodes, or, more frequently, for a constant polarization of the cathode. In the latter cases, at all temperatures, the cathode potential was kept at a lower value than the equilibrium value for a given metal in the same solution, by a constant amount Δ E. The electrolytes used were pure salt solution, and solutions of the same salts with additions of acids or materials which maintain a definite pH value. Some of the experimental results are given in Table 1.

TABLE 1

Electrolysis of Various Salts

Salt concentration in mol/liter	Additive	Temperature, range observed	Maximum observed	Potential in Volts	Polarization E in m.v.	Nature of deposit
$CuSO_4$ 10^{-2}	0,075*M* H_2SO_4	18° boil.	None	2.00 const.	—	Shining
$CuSO_4$ 10^{-2}	0,075*M* H_2SO_4	40—87°	»	1.77	50 const.	Light
$CuSO_4$ 10^{-2}	None	35—95°	76°		100 const.	Darkens
$CuSO_4$ 10^{-1}	10^{-1}*M* H_2SO_4	30—98°	None	1.74	100 const.	Light Shining
$CuSO_4$ 10^{-1}	None	37—91°	85°		50 const.	Darkens
$CuSO_4$ 10^{-1}	»	40—90°	61°		100 const.	»
$CuSO_4$ 10^{-1}	»	18—58°	69°		35 const.	»
$CuSO_4$ 10^{-1}	»	47—80°	75°		50 const.	»
$CuSO_4$ 10^{-2}	0,075*M* H_2SO_4	42—94°	None		100 const.	»
$CuSO_4$ 10^{-2}	10^{-1}*M* H_2SO_4	25—90°	»	1.78	100 const.	»
$CuSO_4$ 10^{-2}	0,075*M*	32—95°	»	1.84—	100 const.	»
$CdSO_4$ 10^{-1}	0.67g $NaHC_4H_4O_6$ 2.7 g Na_2SO_4	20—93°	»	2.10	50 const.	Light Shining
$CdSO_4$ 10^{-1}	None	20—98°	»		50 const.	
$CdSO_4$ 10^{-1}	0.67g $NaHC_4H_4O_6$ 2.7 g Na_2SO_4	33—100°	»		40	Light
$CdSO_4$ 10^{-1}	None	40—88°	»		40	
$AgNO_3$ 100 ml 2.10^{-2}	5 ml 2*N* HNO_3	21—99°	»	1.50 const.		
$AgNO_3$ 2.10^{-2} 100 ml	5 ml 2*N* HNO_3	35—100°	»		40 const.	
$AgNO_3$ 2.10^{-2} 100 ml	10 ml 2*N* HNO_3	40—90°	»	1.60 const.		
$AgNO_3$ 2.10^{-2}	None		85°	1.50 const.		
$AgNO_3$ 2.10^{-2}	»		90°	1.50		
$AgNO_3$ 2.10^{-2} 100 ml	5 ml 2*N* HNO_3	52—100°	None	1 45		
$AgNO_3$ 2.10^{-2} 100 ml	5 ml 2*N* HNO_3	44—100°	»	1.50		

Examples which illustrate the shape of the curves logarithm $I - t^{\circ}$ and logarithm $I - 1/T$ for differing electrolyte composition, are given on the diagrams (Figs. 1, 2, and 3). In these experiments the current was measured one minute after applying the potential to the electrodes and regulating the potential.

DISCUSSION OF RESULTS

Experimental results clearly indicate the relation between the character of the deposition process and electrolyte composition.

When the composition of the electrolyte is maintained so that the electrode process is the same at all temperatures, it was established that, a relation approximately corresponding to Equation (1) was systematically observed. In certain cases, curves with maxima corresponding to those obtained by S. V. Gorbachev and E. P. Starostenko were also obtained; this proved to be clearly dependant on insufficient acidity of the solution. Curves with maxima and the deviations from regular behavior (1a), with respect to current strength, were only obtained in solutions of salt not containing any additives regulating the pH, and other precipitation conditions.

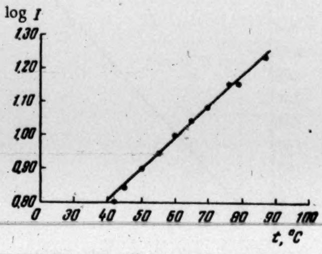


Fig. 1

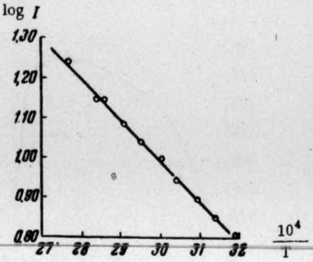


Fig. 2

Figs. 1 and 2. Electro-deposition of copper from a solution of $CuO_4 10^{-2}$ M + 0.075M H_2SO_4 (ΔE = 100 mv constant)

As can be seen from Fig. 1 (electrolysis with acidified solution) in the diagram logarithm I − t°, the arrangement of the experimental points for logarithm I, approximates to a straight line which can be expressed by Equation (1a).

On plotting the same results on the diagram logarithm I–1/ T (Fig. 2), one gets a fair approximation to a straight line again, which can be expressed by the equation:

$$\log I = A - \frac{B}{T}, \tag{3}$$

in which, according to experimental results B = ~ 1,000.

Equation (3) was also found by Gorbachev [7], who, however, reckoned that it was applicable exclusively to electrolysis without deposition of a solid phase (see above). The value calculated theoretically by Gorbachev for aqueous solutions was 445, which is the value also given by Equation (2). It should be pointed out that S. V. Gorbachev's experimental results on electrolysis without deposition of a solid phase also led to a value for B of ~ 1,000, which is more than double the theoretical value (this is pointed out in S. V. Gorbachev's article). In our experiments which gave curves with a maximum, the character of deposition changed quite clearly on heating (see Table 1 and Fig. 3). Chemical analysis of the copper electrolytic deposit, obtained at high temperatures when the electrolyte was not acidified, showed that apparently it was not pure copper that was precipitated but cuprous oxide; the precipitate weighed more than the copper contained in it, e.g. of 112 mg deposit obtained, only 98 mg was copper. Such results may be considered to be a consequence of an increase in hydrolysis at elevated temperature and a shift in the equilibrium for the process:

$$Cu^{2+} + HOH \rightleftharpoons CuOH^{+} + H^{+}.$$

Under these conditions, the following electrode reactions are possible:

1. $Cu^{2+} + 2e = Cu$
2. $Cu^{2+} + e = Cu^{+}$
3. $Cu^{2+} + Cu = 2Cu^{+}$
4. $2CuOH^{+} + 2e = Cu_2O + H_2O$.

The last reaction should become increasingly stronger on increasing the temperature, if the electrolyte is not acidified enough. Similar phenomena have been described in the literature [10] for $CuSO_4$ solutions. Attention should be given to the fact that on dropping the current and increasing the temperature, the potential across the electrodes also drops appreciably (e.g. in one experiment to 1.28 V at 38°). Thus, one of the chief reasons for the appearance of a maximum on the curves, seems to be, apparently, the occurrence of different electrode processes at different temperatures in the same original solution. In view of this, the electro-deposition curves of S. V. Gorbachev and E. P. Starostenko must be regarded as special cases, and are not suitable for

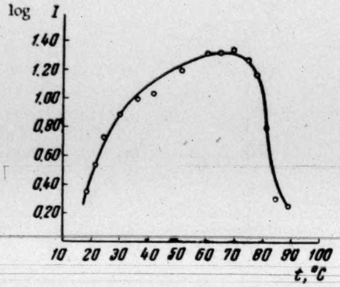


Fig. 3. Electro-deposition of copper from a solution of $CuSO_4 \cdot 10^{-2}M$ (without additives) (ΔE = 35 mv constant).

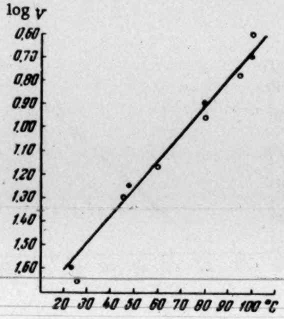


Fig. 4. Logarithm of rate of analysis v as a function of temperature.

for drawing general conclusions in electro-analysis. Our experimental results show that the same electro-crystallization process of a given metal at various temperatures will occur for simple salts, only under conditions where the corresponding acidity is maintained, and also on addition of complex forming salts which protect them from possible hydrolysis, which increases on heating. In experiments on electro-crystallization of copper from an acidified solution, carried out at constant polarization, precipitation of pure copper occurred at all temperatures—the precipitate remained bright, metallic, and shining. The curves logarithm I–t° approximate to a striaght line without any signs of a maximum. In experiments where the electrolyte was not acidified, the character of the deposit changed markedly on raising the temperature—the precipitate became dull, dark red, and even slightly violet.

Logarithmic equations for the straight lines (1a) and (3), correspond, strictly speaking, to distinct rules (since T = 273 + t°), but it is easy to show that within the temperature limits 20 to 100°, these equations, which differ in form, express, reasonably approximately, the general rule of increasing rate of metal deposition (current strength) on heating.

Let us make $T = T_0 + t$, where $T_0 = 273° =$ constant and t, the temperature in °C, when $\frac{1}{T} = \frac{1}{T_0 + t}$.

Resolving 1/T into series:

$$\frac{1}{T} = \frac{1}{T_0} - \frac{t}{T_0^2} + \frac{t^2}{T_0^3} - \frac{t^3}{T_1^4} + \dots$$

For an approximate solution we can take the first 2 members, corresponding approximately to 1/T, and substituting them in (3), we get:

$$\log I = A - \frac{B}{T} = A - B\left(\frac{1}{T_0} - \frac{t}{T_0^2}\right) = a + bt.$$

The differences in the results obtained by calculating the value of the current by means of Formulas (1a) and (3), respectively, will not be very significant, and will be noticeable only at very high temperatures. In practical electro-analysis, these deviations are not of very great significance—experimental results confirm this.

Significance of the Results Obtained for Practical Electro-Analysis

In order to verify and confirm the significance of the results obtained in practical electro-analysis, a series of experiments with Winkler electrodes (without stirrers) was carried out as well as a quantitative electrodeposition of copper from an acidified solution at various temperatures. The rate of the process was determined in relation to the temperature and the time necessary for deposition of copper ions from a solution of the given concentration. The minimum time necessary for complete deposition of copper at various temperatures was observed. The electrolyte was 10^{-2} M $CuSO_4$ + 0.25 N H_2SO_4. After definite time intervals (5, 1, or 0.5 minutes) 1 ml aliquot was taken and tested with $K_4Fe(CN)_6$ for completeness of deposition.

TABLE 2

Duration of Electrolysis in Relation to Temperature and Voltage *

Potential in V	Temperature in °C	Duration in in minutes (a)	Rate $v = \frac{1}{a}$	log v
2.2	26	45	0.022	—1.66
2.2	46	20	0.050	—1.80
2.2	60	15	0.067	—1.17
2.2	30	9	0.111	—0.96
2.2	95	6	0.167	—0.78
2.2	100	4	0.250	—0.60
2.6	23	40	0.025	—1.60
2.6	48	18	0.055	—1.26
2.6	80	8	0.125	—0.90
2.6	100	5	0.200	—0.70

* Analysis was carried out without the use of mechanical stirrer. The electrolyte was 10^{-2} M $CuSO_4$ + $2.5 \cdot 10^{-1}$ N H_2SO_4. Winkler electrodes. In each case mean values of two determinations are given.

In Table 2, in addition to duration of electro-analysis (a), results are also given for the rate; the value v = 1/a, is the reciprocal of the duration of the electro-deposition process. The logarithms of these values, when plotted on a graph of logarithm v – t°, indicate an arrangement more or less approximating to a striaght line (Fig. 4).

Under conditions employed during practical electro-analysis till complete deposition of the cation to be deposited was achieved, it became quite clear that the logarithmic relation established above holds.

Equations (1) and (3), which have been found, should be of practical value in accelerated electro-analysis.

SUMMARY

1. Electro-deposition rate (current strength) as a function of temperature, under such conditions that the electrode process remains the same, can be expressed by the equations: $\log I = a + bt$ or $\log I = A - \frac{B}{T}$; where t is the temperature in °C; T, the absolute temperature. Within the limits 20-100°, these equations represent approximately the same regularity.

2. It is considered that the optimum temperature for speeding up electro-deposition of metal is the temperature at which the electrolyte boils.

3. The occurrence of maxima which were obtained on the deposition curves for copper from non-acidified cupric sulfate solutions by S. V. Gorbachev and E. P. Starostenko is not a general phenomenon; they can be explained by the effect of hydrolysis which becomes more intense on increasing the temperature, and leads to a change in the electrode process—to precipitation of cuprous oxide instead of copper on the cathode.

Received November 26, 1951

LITERATURE CITED

[1] V. A. Karnitsky, Sci. Proc. Rostov-on-Don State University, Chem. Faculty 1939, No. 2, pp. 35-57.

[2] V. A. Karnitsky, Factory Lab. 10, 265 (1941).

[3] V. A. Karnitsky, Bull. Mendeleev Chem. Soc. 5, 31 (1940).

[4] V. A. Karnitsky, "Rate of electrodeposition in relation to temperature", Report given at the Northern Branch of the Mendeleev Chem. Soc. 29, IX. 1934, Reports of the Scientific Work of Members of the Mendeleev Chem. Soc. 1947, No. 1, p. 32.

[5] I. F. Kamyshnikov, Reports of the Scientific Work of Members of the Mendeleev Chem. Soc. 1947, No. 1. p. 30.

[6] P. N. Kovalenko and A. F. Aryeva, Sci. Proc. Rostov-on-Don State University, Chem. Faculty 1947, No. 4, p. 77.

[7] S. V. Gorbachev, J. Phys. Chem. 24, 881 (1950).

[8] A. Fisher and A. Shleikher, Electroanalysis (United Sci. -Tech. Press, Leningrad, 1934).

[9] A. Klassen, Electroanalysis (United Sci. -Tech. Press, Moscow-Leningrad, 1934).

[10] E. Foerster, Elektrochemie Wasseriger Losungen (Leipzig, 1923), Vol. I, p. 502.

ANALYSIS OF HYPOCHLORITES AND CHLORITES IN SOLUTION

I. E. Flis and M. K. Bynyaeva

The V. M. Molotov Leningrad Technological Institute

During bleaching of cellulose and cloth, and also in various other cases, solutions containing both hypochlorites and chlorites at the same time, are used. According to published data [1-3], such solutions are comparatively stable when they are alkaline and can be kept without appreciable decomposition for a fairly long time. In this connection the development of a method for simultaneous determination of hypochlorites and chlorites may be of practical importance.

Carlson and Gelnaar [4], suggested determination of hypochlorite in the presence of chlorite by means of arsenious acid, on the basis that hypochlorite, in contrast to chlorite, rapidly and quantitatively reacts with arsenites. According to their method, an excess of arsenious acid is added to the solution containing hypochlorite and chlorite, and titration with iodine carried out. Hypochlorite content is calculated from the difference between the amount of arsenious acid added and that found by back titration with iodine. According to Carlson and Gelnaar's method, the chlorite is titrated by means of indigo in another aliquot of solution in which the hypochlorite has been decomposed beforehand by arsenious acid.

Later, Foerster and Dolch [2], and also Chapin [3], determined chlorite iodometrically after decomposition of hypochlorite with arsenious acid.

In connection with the methods indicated above, it should be noted that chlorite can oxidize arsenious acid at an appreciable rate in a sufficiently acid medium; secondly, the arsenious acid formed during reaction with hypochlorites can oxidize iodides in acid media. It follows from what has been said that simultaneous determination of hypochlorites and chlorites by means of arsenites and iodometry cannot always give reliable results. It should also be noted that the known variants for the chemical analysis of hypochlorites by means of arsenious acid are fairly tedious, and are, accordingly, not very suitable for practical work [5]. In this case, apparently, a potentiometric method should simplify the analytical technique considerably, and, at the same time, make it more accurate. All the same, despite the appearance of a number of articles devoted to this question, potentiometric analysis of solutions containing hypochlorites and chlorites at the same time cannot be regarded as having been satisfactorily worked out.

Thus, Schleicher and Wesly [6] titrated hypochlorite potentiometrically in the presence of chlorite with arsenious acid, using a platinum electrode; no indications are given in their article of the conditions used or the accuracy of the results they got. In order to get reliable results however it is essential that certain conditions be fulfilled. Thus, e.g. titration in a neutral medium is complicated by side reactions between hypochlorites and chlorites [1], [7]:

$$3ClO_2^- + 2HClO \longrightarrow 2Cl^- + ClO_3^- + 2ClO_2 + H_2O.$$

Muller and Dietmann [7], suggested sodium sulfite for potentiometric titration in a weakly alkaline medium. Their paper again contains no information on conditions, technique, and accuracy of the method they suggest.

Weiner [8], suggested potentiometric titration of chlorite with ferrous salts; from his results it can be concluded that the method gives correct results if the solution is acid enough. Weiner's method cannot be used for solutions containing chlorite at the same time as hypochlorite, in view of the instability of such a system on acidification.

Results are given in the present article of a study of the conditions required for potentiometric analysis of hypochlorites and chlorites when sodium sulfite and arsenious acid are used.

Both test materials were prepared from chemically pure (analytical grade) starting materials.

The hypochlorite was prepared by saturating a solution of sodium hydroxide with chlorine. Chlorine was prepared by reaction of potassium permanganate with hydrochloric acid, and was purified by the usual method before passage through the sodium hydroxide. The original hypochlorite solution contained a certain excess of alkali, an appreciable amount of chloride, but was free from chlorate.

Chlorite was prepared by interaction of chlorine dioxide in solution with sodium and barium peroxides. Chlorine dioxide was prepared by the normal method from chemically pure chlorate , oxalic acid, and sulfuric acid. Chlorine dioxide was freed from impurites before absorption in water, by liquefying it. The liquid chlorine dioxide was evaporated and adsorbed in twice distilled water. The original chlorite solutions were also alkaline. They were practically free from carbonates, chlorates, and chlorides. One of the most essential factors which determines the rate and character of the oxidizing action of hypochlorites and chlorites, is the active acidity of the medium [9-11]. Accordingly, we carried out a series of potentiometric titrations of test solutions acidified to varying extents. All titrations were carried out at a temperature of 18-20° on a Raps type potentiometer. A smooth platinum plate or a platinum net served as indicator electrode. A saturated calomel electrode was used as reference electrode.

TABLE 1

Gram -equivalents of chlorite		Relative deviation of results in %	pH
Iodometry	Potentiometry		
0.000740	0.000740	0.0	6.5—7.0
0.000555	0.000550	—0.9	4.0
0.000710	0.000710	0.0	5.0 (Bicarbonate was added to the solution)
0.000545	0.000550	+0.9	5.5 (The solution contained bicarbonate)
0.000940	0.000925	—1.6	3.5—3.0
0.001360	0.001325	—2.6	2.5—2.0
0.00695	0.000660	—5.0	<2.0

Results for potentiometric titration of chlorite solutions with sodium sulfite are given in Table 1.

Since alkaline solutions of chlorites react comparatively slowly with sulfite, potentiometric titration of such solutions is difficult. Acidified chlorite solutions react readily with sulfite and their potentiometric analysis can be carried out easily and comparatively rapidly.

Sulfite solutions are unstable; accordingly, their concentration was determined before each experiment. A potentiometric titration curve is given in Fig. 1.

It is clear from the results given in Table 1 that on acidifying the chlorite solution to a pH value less than 4 ($pH_< 3.5$), the deviation between iodometric and potentiometric methods is very considerable. The most reliable results are obtained on titrating chlorites in a neutral and weakly acid medium (pH ~ 7-4.0).

Presence of carbonate in solution does not interfere with potentiometric analysis, in complete agreement with Muller and Dietmann's conclusions [7]. It should be pointed out that in the absence of carbonates the E. M. F. is established more quickly.

Subsequently a series of potentiometric titrations were carried out on hypochlorite solution with sodium sulfite, the solution being acidified beforehand to various extents (Table 2 and Fig. 2).

The results given above allow one to conclude that weakly alkaline and weakly acid media (pH 5-8) seem to be optimum for potentiometric titration of hypochlorite with sodium sulfite.

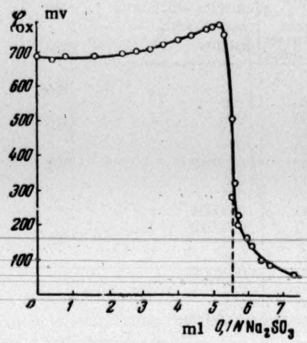


Fig. 1. Potentiometric titration curve of chlorite solution with sodium sulfite.

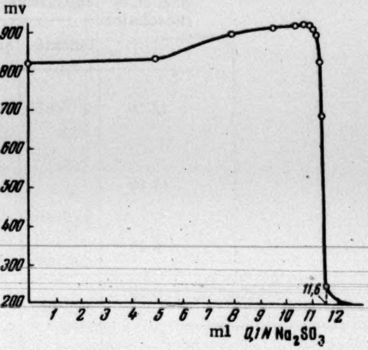


Fig. 2. Curve for potentiometric titration of hypochlorite solution with sodium sulfite

Nevertheless, solutions containing hypochlorites and chlorites are very unstable in weakly alkaline, neutral, and weakly acid media. Accordingly, potentiometric titration with sulfite when both hypochlorite and chlorite are present together can hardly lead to reliable results.

In our next series of experiments with arsenious acid it was taken into account that the systems which we studied are only stable in alkaline media, and simultaneous determination of hypochlorites and chlorites is of practical interest only under such conditions where it is possible to carry out an exact determination of one of them, or of both materials in alkaline solutions.

In order to find out the conditions for analyzing our system by means of arsenious acid, a series of tests were carried out on a study of the rate of interaction of chlorite with arsenite in an alkaline medium. Subsequently, potentiometric titrations of solutions containing hypochlorite and also mixtures of hypochlorite and chlorite (Table 3) were carried out.

It is evident from the results given in Table 3 that in alkaline media, interaction of chlorite with arsenite is slow. In all the cases we studied, a decrease in the chlorite content was not observed over a period of one hour. This leads one to assume that by potentiometric titration in alkaline media, it should be possible to titrate hypochlorite in the presence of chlorite with the help of arsenious acid.

TABLE 2

Gram -equivalents of hypochorite		Relative deviation of results in %	pH
Iodometry	Potentiometry		
0.000550	0.000575	+ 4.5	11.0
0.000575	0.000630	+ 9.5	10.0
0.000670	0.000665	— 0.7	8.5
0.001150	0.001160	+ 0.9	7.0
0.000575	0.000580	+ 0.9	6.5
0.000455	0.000460	+ 1.1	4.0
0.000575	0.000505	—12.2	The solution is strongly acid; pH < 3; chlorine is not evolved from the solution

TABLE 3

pH of the original chlorite solution	Number of gram-equivalents		Time from the point at which the solutions were poured together (minutes)	Number of gram-equivalents of chlorite which have reacted with arsenite
	Chlorite	Arsenite		
12.50	0.000825	0.000500	30	0.0
			60	0.0
			120	0.0
			180	0.0
			2880	0.000120
10.99	0.001630	0.000500	30	0.0
			60	0.0
			180	0.00004
			1560	0.000120
9.70	0.001630	0.000500	30	0.0
			60	0.0
			180	0.000070
8.99	0.001630	0.000500	30	0.0
			60	0.0
			180	0.000070

TABLE 4

Gram-equivalents of hypochlorite		Relative deviation of results in %	Notes
Iodometry	Potentiometry		
0.000225	0.000225	0.0	Solutions contained only hypochlorite
0.001010	0.001015	+0.5	
0.000560	0.000560	0.0	
0.000510	0.000510	0.0	
0.001510	0.001500	—0.6	
0.000595	0.000600	+0.8	Solutions contained hypochlorite and chlorite
0.000935	0.000930	—0.5	
0.001105	0.001105	0.0	
0.001355	0.001345	—0.7	
0.000735	0.000735	0.0	
0.000915	0.000910	—0.5	
0.001190	0.001180	—0.8	
0.001460	0.001450	—0.7	

Results for potentiometric titration of alkaline solutions of hypochlorite with arsenious acid are given in Table 4. On Fig. 3 is shown the potentiometric titration curve of a pure alkaline solution of hypochlorite with arsenious acid, while on Fig. 4 is given a curve for titration of hypochlorite in a solution containing chlorite.

The potentiometric titration results given above confirm that hypochlorite can be titrated with reasonable accuracy by means of arsenious acid in alkaline media containing chlorite.

From an analysis of the potentiometric titration curves (Figs. 3,4) it is clear that, near the equivalence point, there is a fairly clear cut and sharp change in oxidation potential. This allows one to establish the equivalence point easily.

On the basis of our tests and on published data the following method can be recommended for simultaneous determination of hypochlorite and chlorite in solution.

In one aliquot of test solution the total content of hypochlorite plus chlorite is determined iodometrically; in a second aliquot hypochlorite is determined by potentiometric titration with arsenious acid in an alkaline medium (pH > 9).

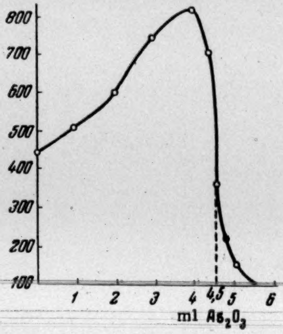


Fig. 3. Potentiometric titration a solution of hypochlorite with arsenious acid.

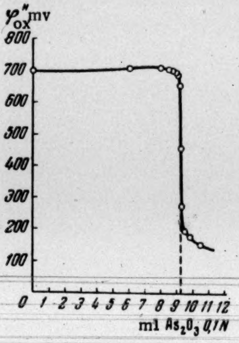


Fig. 4. Potentiometric titration of hypochlorite in a solution containing both chlorite and hypochlorite.

SUMMARY

1. Hypochlorites are best titrated potentiometrically with sodium sulfite at a pH of 5-8, and chlorites at pH 4-7. As a result of the instability of solutions containing a mixture of hypochlorite and chlorite in the pH ranges indicated, sodium sulfite cannot be used for their simultaneous determination by potentiometric titration.

2. It has been established that in alkaline media (pH >9), hypochlorite can be titrated with arsenious acid, in the presence of chlorite, with a fair degree of accuracy.

3. A method is described for simultaneous determination of hypochlorite and chlorite in solution, which is based on a combination of iodometry, and potentiometric titration of an alkaline solution with arsenious acid.

Received February 7, 1955

LITERATURE CITED

[1] J. White, M. Taylor and G. Vincent, Ind. Eng. Chem. 34, 782 (1942).

[2] F. Foerster and P. Dolch, Z. Elektrochem. 23, 137 (1917).

[3] R. Chapin, J. Am. Chem. Soc. 56, 2211 (1934).

[4] B. Carlson and L. Gelnaar, Chem. Ztg. 51, 633 (1908).

[5] K. Shvalbe and L. Ziber, Chemical Production Control in the Cellulose-Paper Industry (State Tech. Forestry Lit. Press, 1934), p. 300.

[6] A. Schleicher and W. Wesly, Z. anal. Chem. 65, 408 (1924-25).

[7] E. Muller and H. Dietmann, Z. anal. Chem. 73, 138 (1928).

[8] F. Weiner, Z. Elektrochem. 52, 234 (1948).

[9] B. P. Nikolsky and I. E. Flis, J. Gen. Chem. 22, 1298 (1952) (T.p. 1343)*.

[10] W. Hisey and C. Koon, Paper Trade J. 36, 103 (1936).

[11] G. Holst, Svensk Pappersmasse-Tidn. 48, No. 2, 24 (1945).

---

* T.p. = C. B. Translation pagination.

BLANK
PAGE

AMPEROMETRIC TITRATION OF ALDEHYDE WITH 2,4-DINITROPHENYLHYDRAZONE

E. V. Zobov and Yu. S. Lyalikov*

Kishinev State University

Amperometric titration of metal ions with inorganic and organic precipitants has been described in detail in a number of articles [1,2]; the equivalence points are determined in such cases by the height of the wave of the precipitant or precipitated ion. We were interested in the possibility of using amperometric titration for determining organic materials, in particular, aldehydes and ketones, as a method which possesses a high degree of accuracy in comparison with others.

We chose 2,4-dinitrophenylhydrazine as precipitant since it readily precipitates, in alcoholic media, a number of aldehydes and ketones in the form of 2,4-dinitrophenylhydrazones. The presence of two nitro groups allows one to assume that 2,4-dinitrophenylhydrazine will be reduced on a mercury cathode.

Studies of the reducibility of 2,4-dinitrophenylhydrazine, and of amperometric titration were carried out on a visual type polarograph with a galvanometer which had a sensitivity of 10^{-9} A. The capillary characteristics were as follows: $m^{2/3} t^{1/6} = 1.275$ mg $^{2/3}$ sec. $^{1/6}$.

Determinations were carried out in these supporting electrolytes: a 75% alcohol solution of 0.05 N H_2SO_4, 0.05 N NH_4Cl, and 0.05 N NH_4OH at a temperature of 18-20°.

The melting point of the 2,4-dinitrophenylhydrazine used was 196°. The reagent was prepared according to a method described by Schriner and Fuson [3]. 0.45 g of 2,4-dinitrophenylhydrazine was introduced into a 25 ml standard flask, 2 ml of concentrated H_2SO_4 added, and, after mixing, 3 ml of water added. When the hydrazine had dissolved, to the still warm solution was added 10 ml of alcohol, then, when the solution had cooled, the solution was made up to the mark with alcohol.

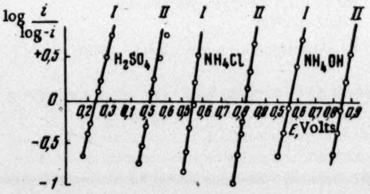


Fig. 1. Determination of the half-wave potential of 2,4-dinitrophenylhydrazine during reduction in H_2SO_4 0.05 N, NH_4Cl 0.05 N and NH_4OH 0.05 N.

It was found experimentally that 2,4-dinitrophenylhydrazine in a supporting electrolyte of H_2SO_4 gives two waves with $E^1_{1/2} = -0.244$ V and $E^2_{1/2} = -0.510$ V. When the supporting electrolyte was NH_4Cl, the half-wave potentials were displaced towards the negative side and became respectively $E^1_{1/2} = -0.546$ V and $E^2_{1/2} = -0.808$ V. In NH_4OH as supporting electrolyte $E^1_{1/2} = -0.566$ V and $E^2_{1/2} = -0.828$ V. All potentials were measured relative to a normal calomel half-element. Half-wave potentials were determined graphically (Fig. 1).

The slopes of the straight lines in the system

$E - \log \dfrac{i}{i_d - i}$ in H_2SO_4 as supporting electrolyte, were 0.09 and 0.075 respectively, in NH_4Cl as supporting electrolyte 0.062 and 0.069, and in a supporting electrolyte of NH_4OH 0.100 and 0.090 for the first and second waves in each case.

When H_2SO_4 was used as supporting electrolyte, a proportionality was observed between each of the waves

---

* Student Derkautsan participated in the experimental work.

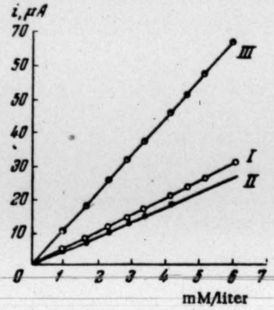


Fig. 2. Calibration curve for 2,4-dinitrophenylhydrazine during reduction in H_2SO_4, 0.05 N for the sum of the two waves.

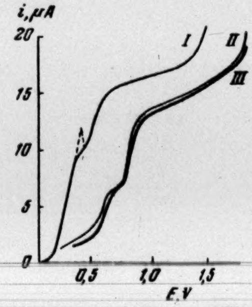


Fig. 3. Reduction wave of 2,4-dinitrophenylhydrazine in a supporting electrolyte of H_2SO_4, 0.05 N.

taken independently, the sum of the two waves, and the concentration $i = KC$ respectively. For the sum of the waves $K = 11.50$ (Fig. 2) in terms of 2,4-dinitrophenylhydrazine at concentrations of 0.15 – 1.30 mM/ liter. The nature of the wave is shown in Fig. 3. Freshly distilled benzaldehyde was used as test material for titration.

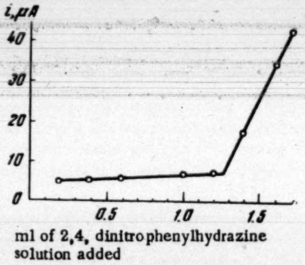


Fig. 4. Titration curve at –0.7 V.

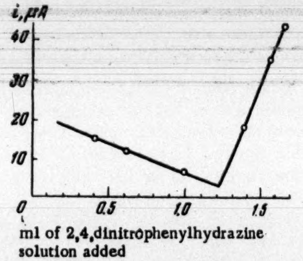


Fig. 5. Titration curve at –1.2 V.

As is evident from the half-wave potentials given above, 2,4-dinitrophenylhydrazine gives a complete polarographic wave at a potential of –0.51 V. Benzaldehyde also gives a wave at a potential of –1.0 V. Amperometric titration of benzaldehyde can be carried out at two constant potentials. When titration is carried out at a potential of –0.7 V, a straight line is first obtained and there is a sharp increase in current after the equivalence point has been reached. The first drops of 2,4-dinitrophenylhydrazine added give a small (up to 7 μA) residual current on account of the small solubility of 2,4-dinitrophenylhydrazine which is reduced at these potentials.

This initial current remains constant during titration up to the equivalence point. The existence of this initial current has no effect on titration results. A titration curve for a potential of –0.07 V is given in Fig. 4.

When titration is carried out at an applied potential of 1.2-1.4 V, which corresponds to the limiting current for the reduction of benzaldehyde, then, at the beginning of titration we get a limiting current which corresponds to the benzaldehyde concentration of the solution. As 2,4-dinitrophenylhydrazine is added, the benzaldehyde wave decreases, while after the equivalence point has been reached, the current starts to increase as a result of increasing 2,4-dinitrophenylhydrazine concentration.

The titration curve obtained under these conditions is shown in Fig. 5.

Amperometric titration was carried out in a supporting electrolyte of a 75% alcoholic solution of 0.05 N H_2SO_4. To 5 ml of the supporting electrolyte was added an alcoholic solution of benzaldehyde, and titration carried out with a solution of 2,4-dinitrophenylhydrazine prepared as described above.

Current was measured at −0.7 V.

Titration of known weights of benzaldehyde in parallel tests, for standardizing a solution of 2,4-dinitrophenylhydrazine gave the following results (Table 1).

TABLE 1

Benzaldehyde taken in g	2,4-Dinitrophenylhydrazine used in ml	Titer (normality)	Mean titer
0.0132	1.50	0.0088	0.0089
0.0132	1.46	0.0090	—

TABLE 2

Benzaldehyde taken in g	2,4-Dinitrophenylhydrazine used in ml	Benzaldehyde found in g	Absolute error in g	Relative error in %
0.00186	0.17	0.00157	0.00029	15.6
0.00373	0.40	0.00373	0.00000	0
0.00559	0.57	0.00532	0.00027	4.8
0.00186	0.19	0.00177	0.00009	4.8
0.02788	2.50	0.0233	0.00466	16.7
0.00935	1.07	0.00941	0.00006	0.7

Mean error 7.1%

It is clear from Table 1 that parallel titrations give results which are in good agreement. Results of titration of arbitrary amounts of benzaldehyde are given in Table 2.

The method is very rapid. A determination takes 11 minutes. As can be seen from Table 2, the results obtained were completely satisfactory. It is possible that this method may find application for other organic compounds containing carbonyl groups.

SUMMARY

1. The polarographic properties of 2,4-dinitrophenylhydrazine have been studied.

2. The applicability of 2,4-dinitrophenylhydrazine to the determination of benzaldehyde by means of amperometric titration has been demonstrated.

Received June 18, 1954

LITERATURE CITED

[1] I. M. Kolthoff and J. J. Lingein, Polarography (State Chem. Press, Moscow-Leningrad, 1948).

[2] T. K. Musina, The Application of Certain Organic Compounds for Amperometric Titration, Author's Thesis (Alma-Ata, 1952).

[3] R. Schriner and R. Fuson, Systematic Qualitative Analysis of Organic Compounds (Foreign Lit. Press, Moscow, 1950).

BLANK
PAGE

DETERMINATION OF SMALL AMOUNTS OF ACIDS AND WATER IN POLYORGANOSILOXANE COMPOUNDS

S. V. Syavitsillo, B. E. Berezovskaya, N. I. Grinkevich, and O. V. Kloptsova

During preparation of polyorganosiloxane compounds, small amounts ($1 \cdot 10^{-3}$ - $1 \cdot 10^{-5}$%) of hydrochloric and sulfuric acids, and water, may get into the end product and lead to corrosion. There are no published methods for determination of these impurities in silico-organic compounds.

Direct titration with an alcoholic solution of alkali for determining total acidity of polyorganosiloxane compounds is not suitable, on account of the low sensitivity. Accordingly, we decided to determine the pH of aqueous extracts of test silico-organic compounds. We were unable to determine the pH of the polyorganosiloxane compounds themselves directly on a type LP-3 pH-meter, using a glass electrode, Separate determination of HCl and H_2SO_4 was carried out nephelometrically [1]. In order to determine small amounts of water in the polyorganosiloxane compounds, we used the hydride method for determination of moisture in petroleum products [2]; this latter is based on measuring the volume of hydrogen liberated during the reaction:

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2.$$

EXPERIMENTAL

The pH of aqueous extracts of the polyorganosiloxane compounds was determined on a P-4 potentiometer (Moskip factory) using a quinhydrone electrode. In order to cut down the viscosity of the polyorganosiloxane compounds before extraction of acid, they were diluted with n-heptane in the ratio of 1:1 (by volume), The distilled water used for extraction was redistilled and had a pH of 6.5-7.

TABLE 1

pH of an aqueous solution to which acid has been added	pH of extract of test material	Acids in %		Relative error in determination in %
		Added	Determined	
4.29	4.28	$9.3 \cdot 10^{-3}$	$9.5 \cdot 10^{-3}$	+2
4.29	4.31	$9.3 \cdot 10^{-3}$	$9.0 \cdot 10^{-3}$	—3
4.72	4.74	$3.5 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$	—5
5.67	5.63	$4.0 \cdot 10^{-4}$	$4.0 \cdot 10^{-4}$	0

It was established that for complete extraction of acid it is sufficient to shake up 20 g of test sample in a separating funnel, with three lots of water, taking 10 ml of water for the first two extracts, and 20 ml for the third extraction. The water extracts were combined and the pH determined. The reliability of the method chosen was checked on synthetic mixtures. For this purpose, a known volume of a standard solution of hydrochloric or sulfuric acid was added to a test sample of polyorganosiloxane compound, diluted beforehand with n-heptane, for which the pH had been determined earlier by water extraction. Water extraction of the acids added was then carried out.

The pH of 40 ml of the aqueous solution of acid, and that of 40 ml of the aqueous extract from the test sample of the polyorganosiloxane compound to which this acid had been added, were then determined separately.

The results obtained are given in Table 1.

It is clear from these results that the acid added to the polyorganosiloxane compounds has been completely extracted and determined by the method just desbribed.

To determine hydrochloric acid, the aqueous extracts from 20 g of test sample were collected in a 50 ml standard flask; from this, 15 ml of solution was transferred to a nephelometric cylinder, and 2 ml of a 10% solution of nitric acid and 2 ml of 0.005 N silver nitrate added. Simultaneously, a series of standards were prepared from potassium chloride, varying in concentration from 0.01 to 0.001 mg of Cl', to which were added the same amount of 10% nitric acid and 0.005 N silver nitrate that was added to the aqueous extract from test sample.

TABLE 2

HCl added in %	HCl determined in %	Relative experimental error in %
$9 \cdot 10^{-5}$	$9 \cdot 10^{-5}$	0
$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	0
$5 \cdot 10^{-4}$	$4.5 \cdot 10^{-4}$	—11
$2 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	—10

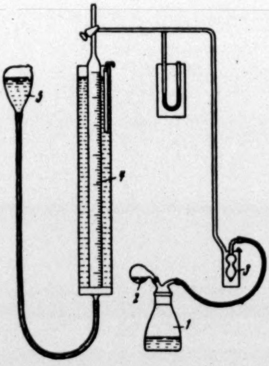
TABLE 3

H_2SO_4 added in %	H_2SO_4 determined in %	Relative experimental error in %
$4.2 \cdot 10^{-4}$	$4.8 \cdot 10^{-4}$	+14.3
$8.9 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	+12.4
$1.36 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	+10.1
$1.32 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	— 5.3

The solutions in all the nephelometric cylinders were mixed and the intensity of the turbidity formed compared on a black background after 10 minutes.

The correctness of hydrochloric acid determination by means of the method indicated was checked on analyses of synthetically prepared test samples (Table 2).

The results in Table 2 show that the accuracy of the determination amounts to 11% relative. The sensitivity of the method if one takes a sample of 20 g is $9.0 \cdot 10^{-5}$%.



Apparatus for moisture determination

H_2SO_4 was determined by transferring 10 ml of the 50 ml combined aqueous extracts to a nephelometric cylinder, to which was then added 0.5 ml of 0.1 N hydrochloric acid containing 14 g of sodium chloride per 100 ml solution, 1 ml of 10% barium chloride solution, and 8 ml of water.

Standard solutions were prepared at the same time containing 0.02 to 0.1 mg of SO_4^{2-}. After mixing, the turbidity formed in the extracts from test sample was compared after 10 minutes, with that of standard solutions. In addition, a blank test was made in which 10 ml of aqueous extract was treated with all the reagents indicated except barium chloride.

The value obtained for the blank was subtracted from the respective amounts of SO_4^{2-} found.

This method was also shown to be suitable by carrying out analysis of synthetic mixtures; results for these tests are given in Table 3.

These results show that experimental accuracy amounts to 14% relative, while the sensitivity for an aliquot of 20 g is $4.0 \cdot 10^{-4}$%.

Water was determined in the apparatus shown in the diagram. 100 g of test material was introduced into the reaction flask 1, which has a side flask 2 for calcium hydride. Reaction flask 1 was connected with a bubble counter 3 filled with sulfuric acid, which, in its turn, was connected with a gas buret 4. Into 2, by means of a funnel was introduced ~1 g of calcium hydride. The apparatus was then checked to see if it was hermetically sealed, after which the calcium hydride was gradually introduced into the reaction flask containing test sample, by rotating the neck of the flask in the ground glass joint. When hydrogen had ceased to be evolved the level of the water in the levelling tube and the buret were levelled and the volume of hydrogen measured.

Water content was calculated by means of the formula:

$$c = \frac{0.000805 \cdot V_0 \cdot 100}{a} \%,$$

where 0.000805 is the amount of water in g corresponding to 1 ml of hydrogen under normal conditions; V_0, volume of hydrogen evolved in ml under normal conditions; a, weight of test sample in g.

TABLE 4

Water added in %	Water determination in %	Relative experimental error in %
$3.0 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$	+10
$6.4 \cdot 10^{-3}$	$6.4 \cdot 10^{-3}$	0
$5.7 \cdot 10^{-3}$	$5.5 \cdot 10^{-3}$	− 3.5
$1.75 \cdot 10^{-3}$	$1.79 \cdot 10^{-3}$	+ 2.2
$2.47 \cdot 10^{-3}$	$2.38 \cdot 10^{-3}$	− 3.2

Water was determined in synthetic mixtures by means of this method. Results are given in Table 4.

These results show that accuracy of determination amounts to 10% relative, while sensitivity for a sample weight of 100 g is $1.0 \cdot 10^{-3}$%.

SUMMARY

A method has been developed for determining 10^{-3} to 10^{-5}% of hydrochloric and sulfuric acids, respectively, and water, in polyorganosiloxane compounds with an accuracy of 10-15% relative.

Received March 10, 1955

LITERATURE CITED

[1] D. G. Iou, "Nephelometry", Photometric Chemical Analysis (United Sci. -Tech. Press, 1936), Vol.II.

[2] H. Brochi and W Scheer, Brennstoff-Chem. 13, 281 (1932).

BLANK
PAGE

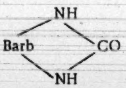
POTENTIOMETRIC INVESTIGATION OF BARBITURATES

PART 2*. EFFECT OF pH ON COMPLEX FORMATION OF BARBITURATES WITH THE SILVER ION

Ya. M. Perelman

Leningrad Institute of Pharmaceutical Chemistry

In the present article we shall deal with barbituric acid derivatives which are not substituted at the nitrogen atom:



In order to establish the nature of the compounds formed, titrations of pure Medinal (the sodium salt of Veronal, diethylbarbituric acid) with silver nitrate were carried out. Experimental conditions and apparatus were identical to those used in previous work (see Part 1)*.

The preparations used satisfied the requirements of the USSR State Pharmacopeia, Seventh edition, and contained 99.3% Medinal. During titration, intially, where each drop of $AgNO_3$ solution fell into the test solution, a turbidity appears which disappears quickly; subsequently, at a certain juncture, a turbidity develops which gets stronger all the time, until eventually a copious precipitate is formed. Fig. 1 represents titration of a 0.0479 M Medinal solution (pH 9.7-9.8). It might be suggested that the first jump corresponds to the completion of formation of a soluble complex at a ratio of 1 mole of silver nitrate to 2 moles of diethylbarbituric acid, while the second one corresponds to completion of formation of an insoluble salt, in which 1 atom of silver corresponds to 1 anion of barbituric acid.

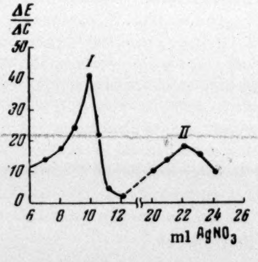


Fig. 1. Titration of 50 ml of 0.0479 mole/liter Medinal with 0.1 N $AgNO_3$: I) [Veronal.Ag]Na + Veronal; II) Veronal. Ag_2 + Veronal.

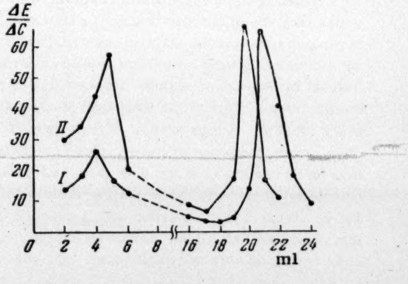


Fig. 2. I) Veronal (0.2088/40) + 1 g borax; II) Veronal (0.1944/20) + 1 g borax + 20 ml alcohol 96%.

---

* Part 1, J. Anal. Chem. 11, 241 (1956) (C. B. Translation p. 243).

Such suggestions are not confirmed experimentally.

0.3858 g of Medinal was dissolved in 30 ml of water in a 100 ml standard flask, to which was then added 50 ml of 0.1 N silver nitrate, 10 ml of 5% barium nitrate (to coagulate the precipitate) and the solution made up to the mark. After shaking, the solution was filtered; 40 ml of filtrate after acidification with HNO_3 was extracted several times with ether. The residue after removal of ether proved to be pure Veronal amounting to 0.065 g, which represented 47.15% of Medinal taken. The filtered precipitate after purification and drying contained 52.67% Ag, i.e. the precipitate in fact corresponds to Veronal.Ag_2. From this, it can be concluded that half of the Medinal did not react during formation of the initial complex, or during formation of the precipitate. The part of the curve before the first maximum indicates, in general, formation of a complex [Veronal.Ag]Na, both during titration in a carbonate medium, and of free barbiturate; the second jump, which is quite small, indicates completion of formation of Veronal.Ag_2, from the fact that only half the Medinal taken reacted. The first jump has no analytical value, it comes too early (see table). The second jump is of great practical interest, but this one again is rather premature, and will naturally lead to low results (1.5-2%). Titration of Medinal in presence of sodium carbonate was similar to results for Veronal. Titration of Veronal in presence of borax is of practical interest.

Satisfactory results are possible even in the cold; for improving titration conditions, calcium carbonate is also added. 0.2-0.25 g of Veronal is dissolved in 40 ml of water; 1.0 g of borax, 0.3 g of calcium carbonate are then added; 0.1 N silver nitrate is added first in 1 ml lots, and then as the equivalence point is reached, it is added in 0.2 ml lots, the potential being measured after each addition. Titration is carried out slowly (the potential is allowed to settle over a period of 2 minutes) and with energetic stirring; at the equivalence point $\Delta E/\Delta C$ is a maximum. 1 ml of 0.1 N solution corresponds to 0.00921 g Veronal or 0.01031 g Medinal.

Potentiometric Titration of Medinal with Silver Nitrate

Concentration of solution being titrated in g/ml	First max. $\frac{\Delta E}{\Delta C}$ when $AgNO_3$ added, ml	Titrated in % (gram-equivalents, 2 mol. Medinal)	Second maximum occurs when the following amounts of $AgNO_3$ added, ml	Titrated in % (gram-equivalents 1 mol of Medinal)	Notes
0.4993/50	10.65	87.96	23.69	97.90	Medinal content 99.3%
0.4993/50	10.50	87.60	23.69	97.90	
0.4942/50	10.60	88.46	23.29	97.20	
0.3148/30	15.25	—	—	99.89	In the presence of 1 g sodium carbonate

When titration is carried out rapidly, the results obtained are low. It should be pointed out however that during slow potentiometric titration, a systematic negative error of 1.1% is obtained. Titration in the presence of alcohol improves the shape of the curve and the position of the first maximum (Fig. 2); nevertheless we did not succeed in getting coincident results when this maximum was used. Thus, by comparing titration of Veronal in presence of sodium carbonate and of borax, one can conclude that the appearance on the potentiometric curve of signs of the formation of one complex or another, depends to a considerable extent on the pH of the medium. A high pH value favors formation of the complex [Veronal.Ag]Na; at lower pH, which borax gives rise to, formation of the complex [$(\text{Veronal})_2$Ag]Na is clearly manifest, and the first does not appear at all. In order to confirm what has been said, Malyl (diallylbarbituric acid) was titrated; in the given instance, this completely reproduces the properties of diethylbarbituric acid. A 0.1 M carbonate solution of Malyl was prepared. 25 ml of Malyl solution with a concentration of 0.0297 mole/liter was taken for titration; borax or sodium carbonate was added in order to change the pH of the solutions. pH was measured by means of a glass electrode on an ultraionograph with a tube voltmeter and direct registration of the E. M. F.

1. Solution with pH 9.2; completion of formation of [$(\text{Malyl})_2$Ag]Na is clearly defined by a rather small maximum; the complex [Malyl.Ag]Na does not appear at all; another maximum indicates formation of Malyl · Ag_2.

2. Solution with pH 10; a jump for [$(\text{Malyl})_2$Ag]Na is absent; an insignificant but quite distinct jump indicates [Malyl.Ag]Na; this however occurs long before the equivalence point (premature decomposition since the pH is not high enough); a second jump corresponds to Malyl.Ag_2.

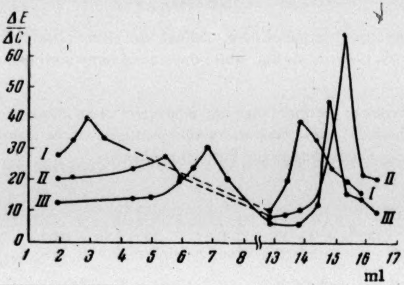


Fig. 3. I) 0.1 N carbonate solution of Malyl (0.0297 mole/ liter) + 0.3 g borax (pH 9.2); II) 0.1 N carbonate solution of Malyl (0.0297mole/liter) + 0.2 g sodium carbonate (pH 10.0); III) 0.1 N carbonate solution of Malyl (0.0297mole/liter) + 1.0 g sodium carbonate (pH 11.2).

3. Solution with pH 11.2; there is no separate jump for $[(\text{Malyl})_2\ \text{Ag}]\text{Na}$; an appreciable jump, in the right place for [Malyl.Ag]Na, and finally, a second jump for Malyl.Ag_2 (Fig. 3). As far as the practical results go, what has been said above for Veronal also holds for Malyl. Titration of Malyl in the presence of sodium carbonate proceeds in the same way as for Veronal. The jump is small, but clearly defined, and allows the equivalence point to be fixed ($K_{\text{instability}}$ $1.1 \cdot 10^{-7}$ at 20°); the second jump which corresponds to the completion of formation of Malyl.Ag_2, is appreciably bigger than in the case of Veronal, and corresponds to the value we found for Solubility Product $_{\text{Malyl.Ag}_2}$ $-0.18 \cdot 10^{-13}$(at 15°), and Solubility Product $_{\text{Veronal.Ag}_2}$ $-6.2 \cdot 10^{-12}$(at 15°).* On Fig. 4 is shown the titration curves of 25 ml of 0.00448 M Malyl in the presence of 0.24 g borax, and of 25 ml of 0.0448 M Malyl solution respectively (the parts of the curves shown, relate to the region of the second potential jump). The gram equivalent is equal to half the molecular weight. Deviations during titration amount to 1-1.5%.

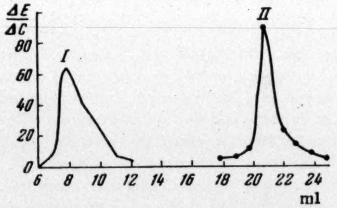


Fig. 4. Titration of Malyl with 0.1 N $AgNO_3$ in the presence of borax: I) 0.00448 M soltion; II) 0.0448 M solution.

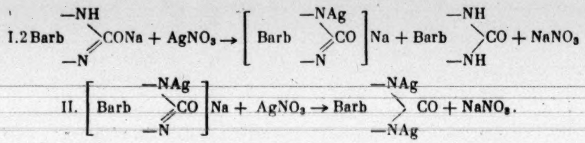
---

* Experimental procedure is described in Part 1.

SUMMARY

1. During potentiometric titration of pure Medinal with silver nitrate, the first potential jump corresponds to formation of the complex [Veronal.Ag]Na, while the second jump corresponds to completion of formation of Veronal.Ag_2.

2. Even in the presence of not more than one equivalent of an alkali metal, an excess of silver nitrate, during the reaction with barbituric acid derivatives not substituted on the nitrogen atom, leads to formation of Barb. Ag_2. Reactions proceed according to the following schemes:



$$\text{I. } 2\,\text{Barb}\begin{matrix}-\text{NH}\\ \rangle\text{CONa}\\ -\text{N}\end{matrix} + \text{AgNO}_3 \rightarrow \left[\text{Barb}\begin{matrix}-\text{NAg}\\ \rangle\text{CO}\\ -\text{N}\end{matrix}\right]\text{Na} + \text{Barb}\begin{matrix}-\text{NH}\\ \rangle\text{CO}\\ -\text{NH}\end{matrix} + \text{NaNO}_3$$

$$\text{II. } \left[\text{Barb}\begin{matrix}-\text{NAg}\\ \rangle\text{CO}\\ -\text{N}\end{matrix}\right]\text{Na} + \text{AgNO}_3 \rightarrow \text{Barb}\begin{matrix}-\text{NAg}\\ \rangle\text{CO}\\ -\text{NAg}\end{matrix} + \text{NaNO}_3.$$

3. Formation of the complex [(Veronal)$_2$ Ag]Na can be followed during titration of Veronal in the presence of borax.

4. Formation of the first or second complex can be followed on the potentiometric curve obtained during titration of barbiturate solutions at varying pH: at a pH of ~ 9.2, the complex [(Barb)$_2$ Ag]Na is formed, while at a pH of 11.2 and higher the complex [Barb.Ag]Na is formed.

5. Formation of Barb.Ag_2 in the cold, during titration of Veronal and Malyl with silver nitrate, can be used as the basis of a practical method for determining barbiturates (the experimental error is ~ 1-1.5%).

6. The calculated value for $K_{\text{instability}}$ of [Malyl.Ag]Na proved to be $1.1 \cdot 10^{-7}$ at 20°, while the value for Solubility Product$_{\text{Malyl.Ag}_2}$ was found to be $0.18 \cdot 10^{-13}$ at 15°.

Received September 8, 1954

A NEW METHOD FOR THE SPECIFIC DETERMINATION OF CHLORINE

L. M. Kulberg*and L. D. Borzova

The N. G. Chernyshevsky Saratov University

Determination of traces of chlorine, which is of particular interest in the analysis of water for domestic and industrial consumption, cannot be considered to be satisfactorily solved at present. All known methods of determining chlorine are based on reversible or irreversible oxidation of inorganic or organic compounds. The reagents used for this purpose are essentially characteristic oxidation- reduction indicators.

In principle one cannot look for an organic oxidation-reduction reagent which would be strongly selective with respect to free chlorine, the hypochlorite ion or hypochlorous acid.

In recent years ways have been pointed out for solving the question of selective determination of oxidizing agents when present simultaneously. Thus, Kulberg [2,3], detected traces of the anions of strong oxidizing agents when present simultaneously, by combining precipitation reactions with oxidation-reduction reaction, and the use of chemical reactions of a synthetic type.

Analytical reactions which are based on the synthesis of new, intensely colored, compounds, are not numerous and are used mainly for detection and determination of inorganic materials of non-salt-like character, in certain cases for the detection of anions, and, very rarely, for detection of cations. As an example one may instance detection of nitrites by diazotization of an amine, followed by combination of the diazonium salt formed with another amine or phenol (Griess reaction); determination of nitrate by means of disulfophenolic acid, on the basis of formation of picric acid [4]; determination of ammonia with hypobromite and thymol as a result of formation of a dye which is colored greenish blue in aqueous solutions, and red in ethereal solution [4]. Kuznetsov's reaction [5], for detecting scandium is a reaction of the synthetic type; it is based on formation of a colored inner complex salt by the action of o-aminophenylarsonic acid and salicylaldehyde on a solution of the scandium salt.

For colorimetric determination of chlorine, only one synthetic reaction is known, viz. that proposed by Milton [6]; this is based on interaction of free chlorine with the cyanides of alkali metals to give quaternary bases, which, on subsequent condensation with aromatic amines, give intensely colored dianil derivatives. According to the author, this reaction is approximately twice as sensitive as the o-toluidine method, and is specific for chlorine in the presence of all oxidizing agents, with the exception of free bromine. A check carried out on chlorinated water, confirmed the high sensitivity of the method, but, at the same time also demonstrated that some chloramines behave just like chlorine [7]. The difficulties connected with the use of this method in its original form for determining chlorine in turbid solutions, and the impossibility of carrying out separate determination of free and combined chlorine led to the use of extraction [8]. This modification permits determination of 0.055 to 1.4 mg/ liter of Cl_2. Maximum color develops after 30 minutes. Standard solutions are prepared from potassium cyanide and bromine water.

A characteristic reaction for chlorine could be worked out in this case, if one could find a synthetic process which would be strictly selective for chlorine, and would be accompanied by quantitative formation of an easily measured reaction product.

Unfortunately, one of the characteristic features of the interaction of organic compounds with chlorine is the occurrence of simultaneous reactions in several directions.

---

* Deceased.

A synthetic reaction which would be of potential use in this respect would be one in the first stage of which the most characteristic chemical feature of chlorine is used, viz. its oxidizing properties; here it is essential to look for an oxidation-reduction process, whose products would give a specific reaction with some reagent.

Compounds containing amino- and hydroxy-groups connected with the aromatic nucleus, are fairly readily oxidized to give colored products. As a result, the reactions which occur between chlorine and other oxidizing agents with aniline and phenol have interested many research workers [9-12]. The development of a blue color which changes into red by the action of chlorine on an aqueous solution of aniline has been used for detecting chlorine. The nature of the colored compound formed has remained unknown. The insignificant sensitivity of this reaction, and the instability of the color developed, has led to the development of another variant which consists in adding a solution of o-toluidine to the aqueous aniline solution [9,10]. This method has only been developed and applied to qualitative detection of chlorine.

In 1891 Denige [11], proposed the use of a mixture of solutions of aniline and phenol instead of just aniline alone for increasing the sensitivity of chlorine detection. This reaction has not yet found appreciable use for qualitative detection of chlorine, although it has been recommended in the second report of the International Commission on New Analytical Reagents as a very good example of a strictly specific reaction for chlorine [13].

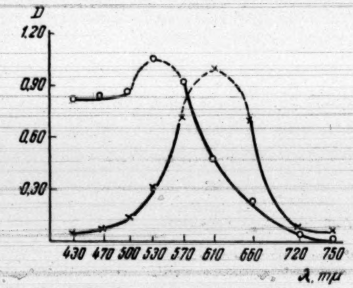


Fig. 1. Light absorption curves for the oxidation products formed by the action of chlorine on an aniline solution, and for the reaction product formed between chlorine, aniline, and phenol in aqueous solutions respectively: o) aniline + chlorine; x) aniline + phenol + chlorine.

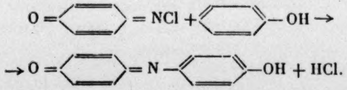
In the International Commission's report it is pointed out that this reaction is based on the "development of a blue color, which is determined by the reaction products of the reagents". This sort of explanation is far from good enough. Aniline in alkaline media, under the influence of hypochlorite, does not give, as can be directly shown experimentally, any intense blue color; under these conditions it is a rose-violet color which is formed which does not remotely resemble the color which develops during the reaction being discussed (Fig. 1). It should be noted that during the action of hypochlorite in alkaline solution on aniline, a color only develops at fairly high hypochlorite concentrations. When solutions containing relatively small amounts of the latter are used, no visible changes occur with an aniline solution. At the same time, phenol in alkaline solution, under the effect of hypochlorite, does not undergo any changes which are accompanied by a color change. Consequently, only the simultaneous presence of aniline and phenol can ensure formation of the characteristic blue color. If this is true, then it is incorrect to say that the color only develops as a result of the oxidation of reaction components; it is quite likely that here in fact we have an instance of an oxidative synthesis. These considerations led us to stage a number of tests in order to find out the mechanism of the reaction.

Oxidation of aniline under rigorous conditions leads mainly to the formation of quinone [14]. It is possible that during the oxidation of aniline by hypochlorite under milder conditions, chlorimine may be formed in the first stage.

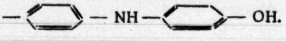
Chlorimine is known to be a very active compound which readily condenses with many compounds. The correctness of the assumption that quinonechlorimine is formed as an intermediate product, is confirmed by the fact that one can prepare indophenol oxidation-reduction indicators by coupling quinonechlorimines with phenols [15].

Burmistrov and Titov [16], have pointed out the instability of quinonechlorimines, and the ease with which they react with phenols and amines to form indophenols and indamines.

Chlorimine readily reacts with phenol to give an intensely colored indophenol according to the equation:



Similar indophenols can be obtained by simultaneous oxidation of two aromatic compounds, one of which contains an amino group, while the other contains a hydroxy, or free, or substituted amino group.

All this leads one to postulate that the mechanism of the reaction under consideration boils down to an oxidative synthesis of quinone-chlorimine, and its subsequent coupling with phenol to form an indophenol. The blue indophenol is the final reaction product, and on the basis of the amount of it formed, and consequently on the basis of the intensity of the color developed, it should be possible to estimate the amount of hypochlorite ion present in the test solution. In acid media, indophenols are red (the undissociated molecule); in alkaline media, as we have already pointed out, they are blue (the dissociated indophenolate). On reduction they form a colorless leuco-compound 

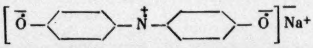
For an explanation of the mechanism of interaction, use was made of the well known fact that agreement between the forms of the light adsorption curves is a convincing proof of the identity of test materials. It was shown [14], that when p-aminophenol is oxidized in acid media with chlorine, with subsequent coupling of the oxidation products with phenol in an alkaline medium, indophenol is formed. The same indophenol should be formed also from aniline and phenol. In order to prove this, indophenol was prepared by oxidizing p-aminophenol as follows: to 1 ml of a solution of p-aminophenol in an acid medium was added 1 ml of chlorine water in 2 ml of phenol solution. After 2-3 minutes a solution of sodium hydroxide was added till a blue color developed. The same product was obtained by following the method given in the report of the Commission [13]. The solutions obtained which were colored blue were diluted with water till their colors were similar when observed visually; absorption curves were then taken for each of the solutions. The curves are illustrated graphically in Fig. 2. The complete agreement obtained between the light absorption curves undoubtedly testifies to the complete identity of the products formed.

In order to confirm the results obtained, similar experiments were carried out with other pairs of amines and phenols:

p-aminophenol - o-cresol; aniline - o-cresol.
p-aminophenol - α-naphthol; aniline - α-naphthol.

The results of these tests are also shown graphically in Fig. 2. Here again the light absorption curves obtained practically coincide with each other.

Thus, it can be assumed, that during interaction of chlorine with aniline in an alkaline medium, the indophenolate



is formed.

We have already pointed out that other amines and other phenols can be used for this reaction instead of aniline and the corresponding phenol.

Results obtained on coupling various amines and phenols are given in Table 1.

It is obvious that the value of the optical density in the given instance simply defines the reaction sensitivity. Consequently, the most sensitive combination is o-cresol - aniline. Nevertheless, since o-cresol is not readily available, we used the pair aniline -α-phenol, which, with respect to sensitivity differs very little from o-cresol.

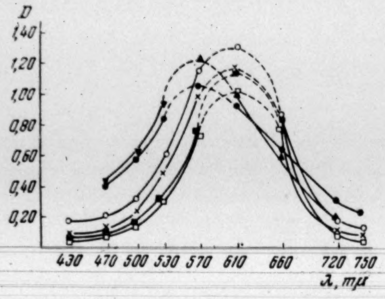


Fig. 2. Light absorption curves for products formed by the interaction of amines and phenols with chlorine: o) aniline + o-cresol + chlorine; x) p-aminophenol + o-cresol + chlorine; ●) aniline + α-naphthol + chlorine; ▲) p-aminophenol + α-naphthol + chlorine; □) aniline + α-phenol + chlorine; ■) aminophenol + phenol + chlorine.

In order to establish the characteristics of the reaction with the idea of using it for quantitative analysis, we first of all studied the effect of the ratios of the concentrations of alkali, phenol, and aniline on reaction sensitivity (the chlorine content was kept constant).

The following procedure was used throughout: a standard solution of chlorine water was mixed with a sodium hydroxide solution of known concentration, and then with known amounts of phenol and aniline. The total volume of all solutions was kept constant. Optical density of solutions was determined after 20 minutes. Measurements were carried out on a photometer, in a cell with l=5 mm at 610 mμ. Sensitivity is characterized by the value D. The effect of phenol concentration was first studied; the order in which the solutions were added to each other was kept the same as recommended for quantitative detection. In this case, to 1 ml of 1N sodium hydroxide was added 1 ml of chlorine water with a concentration of 80 γ/ ml, and 5 ml of an aqueous solution saturated at room temperature with aniline, followed by a known volume of 5 % phenol solution. The total volume was made up to 12 ml. Optical density was determined after 20 minutes.

The results obtained are shown graphically in Fig. 3.

As shown experimentally, maximum values of the optical density are seen at comparatively low values of added phenol. Excess phenol leads to a decrease in the optical density of the solution, while appreciable excess of phenol leads to development of turbidity.

TABLE 1

Effect of the Reaction During Coupling of Various Phenols and Amines

Amines	Phenols	Reaction effect	Optical density Chlorine concentration 70 γ/ml
Aniline	phenol	Blue color	0.72
o-Toluidine	phenol	» »	0,70
m-Toluidine	phenol	» »	0,65
p-Toluidine	phenol	No color develops	—
Dimethyl-p-phenylenediamine	phenol	Blue color, intensity of which increases in air	—
aniline	α-naphthol	Blue color	0.63
aniline	Resorcinol	No color develops	—
aniline	Pyrocatechol	No color develops	—
aniline	8-Hydroxyquinoline	Blue color	0.32
aniline	m-Cresol 1	» »	0.56
aniline	o-Cresol	» »	0.78

Our experiments suggest that at a certain ratio of sodium hypochlorite and phenol, chlorination of the latter occurs, and that this explains the turbidity developed. This circumstance leads to partial loss of chlorine; as a result, the amount of indophenol formed during the reaction decreases, and this in turn leads to low values for the optical density. In subsequent experiments 1 ml of 5% phenol solution was always added.

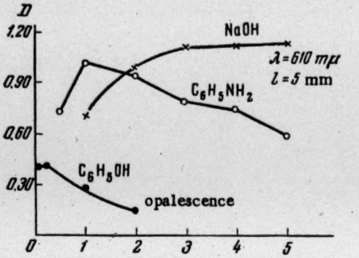


Fig. 3. Effect of the amount of aniline, phenol, and alkali, respectively, on the value of the optical density of solutions of the reaction products formed between aniline, phenol, and chlorine. o) saturated aqueous solution of aniline; x) 0.2 N alkali; ●) 5% phenol.

TABLE 2
Reproducibility of the Results Obtained for Determination of Chlorine When the Indophenol Reaction Is Used

Chlorine concentration in γ/ml taken	Chlorine concentration found in γ/ml	Absolute error in γ
85.0	85.0	0.0
73.0	72.5	—0.5
68.0	69.0	+1.0
60.0	59.0	—1.0
52.0	53.5	+1.5
45.0	42.0	—3.0
40.0	41.0	+1.0

In the next series of tests, 1 ml of chlorine water of the same strength as that used in the preceding experiments was added to 1 ml of 1 N sodium hydroxide; this was followed by varying amounts of a saturated aqueous solution of aniline, and 1 ml of 5% phenol solution. The total volume in all cases amounted to 8 ml. Measurements were carried out as described above. The results obtained are shown in Fig. 3.

According to the results obtained, the amount of aniline which is added is reflected in the value of the optical density. Optimum results were obtained on adding 1 ml of aniline solution.

A number of tests were also carried out in order to establish the effect of the amount of alkali on the course of the process being studied. In this case, the following were introduced into solution: 1 ml of a saturated aqueous solution of aniline, 1 ml of 5% phenol solution, and from 1 to 5 ml of 0.2 N NaOH solution. The results obtained are shown graphically on Fig. 3.

It is obvious that 3 ml of 0.2 N sodium hydroxide ensures that the reaction proceeds to the maximum extent.

Keeping to the favorable ratios of reagents established by us is particularly important in those cases when determinations of traces of chlorine are carried out. When the test material contains a relatively large amount of chlorine, the amount of reagents used—sodium hydroxide, phenol, and aniline—can be altered within a fairly wide range, without having any practical effect on the accuracy of the results obtained. The curve given on Fig. 4 for the ratio of components: 1 ml chlorine water, 1 ml 1 N sodium hydroxide, 2 ml of 3.5% aqueous aniline solution, and 2 ml of 5% phenol solution, serves as confirmation of the correctness of what has been said above.

The use of the curve shown on **Fig. 8 gives results of good reproducibility and reasonable accuracy.** (Table 2).

The order in which the reagents are poured together is an important one. In the absence of other halogens, and during the use of the ratios for the reagents given above, aniline should be added first, and then the phenol. When the order is changed, no color develops (the latter phenomenon is only observed in those cases where a relatively large amount of phenol is introduced into the reaction mixture).

One should not forget either that the reaction under discussion does not proceed instantaneously (Fig. 5). The optical density remains practically unchanged after 20-120 minutes.

The blue color of the solution is stable for a long time.

The specificity of the reaction under discussion is very important. A study of this question showed that manganese (in alkaline solution, actually $MnO_2 \cdot H_2O$), trivalent iron, nitrites, and hydrogen peroxide, and also mono- and dichloramines do not have any observable effect on chlorine determination. Bromine and iodine, as one would expect, give the identical reaction, under the conditions discussed above; Denige's [11] statement that bromine does not react, is incorrect. All the same, the influence of bromine can be completely eliminated by introducing phenol into the reaction medium. It is probable that the sodium hypobromite which is in solution reacts with phenol to form tribromophenol according to the equation

$$C_6H_5OH + 3NaBrO \rightarrow C_6H_2Br_3OH + 3NaOH$$

and is removed from the sphere of action. The fact that the reaction does proceed according to this equation is supported by its use for the quantitative determination of phenol [17]. For a ratio of phenol to aniline of 1:20, the order in which the reagents are added has no effect on the value of the optical density of the solution obtained (even for an insignificant bromine content).

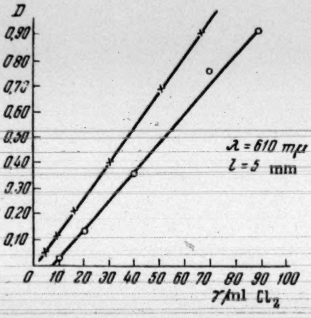


Fig. 4. Calibration curves for determination of chlorine concentrations exceeding 5 γ/ml in the presence, and in the absence of bromine, when using the synthetic reaction: o) bromine absent; x) bromine present.

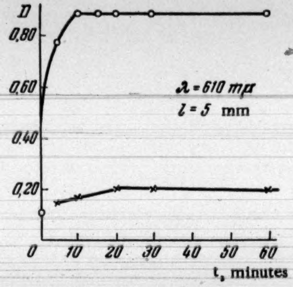


Fig. 5. Effect of time on the value of the optical density of the solution of reaction product, formed during the synthetic reaction (for 15γ/ml Cl_2) in the presence, and in the absence of bromine: x) bromine absent; o) bromine present.

The precipitates of tribromophenol or triiodophenol which are formed in the course of the reaction, in the presence of bromine and iodine respectively, dissolve, and do not interfere with measurements of the value of the optical density.

Experiments carried out with the aim of finding the optimum conditions for determining chlorine in the presence of bromine and iodine, and carried out under the same conditions as those described above (C_{Cl_2} = 60γ/ml), showed that when more than 0.2 ml of a 5% solution of phenol is added, no color develops. Decreasing the amount of phenol to 0.1 ml has no effect on the value of the optical density; accordingly, in subsequent experiments, 0.1 ml of phenol solution was used.

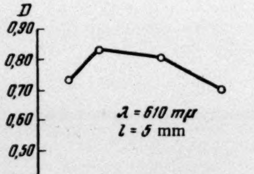


Fig. 6. Effect of the amount of aniline on the value of the optical density of a solution of the reaction product formed between aniline, phenol, and chlorine (determination of chlorine in the presence of bromine).

With respect to the influence of aniline, as can be seen from Fig. 6, the maximum value of the optical density is observed when 1 ml of a saturated solution of the latter is used. It should be pointed ou that within the concentration range of aniline which we studied, we did not detect any effect exerted by aniline on the value of the optical density.

A somewhat different picture is obtained when various amounts of 0.2 N sodium hydroxide are introduced into the reaction solution. In this case, as can be seen from Fig. 7, the maximum value for the optical density is observed when 5 ml of 0.2 N sodium hydroxide solution is added.

Thus, in order to achieve maximum specificity, the following procedure should be followed: to 1 ml of of 1 N sodium hydroxide are added 1 ml of test solution, 0.1 ml of 5% phenol solution, and 1 ml of a saturated aqueous solution of aniline.

Measurement of the optical density, as can be seen from Fig. 5, can then be carried out after only 10 minutes.

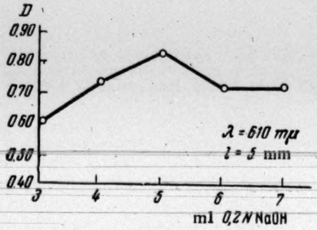


Fig. 7. Effect of the amount of alkali on the value of the optical density of a solution of the reaction product formed between aniline, phenol, and chlorine (determination of chlorine in the presence of bromine).

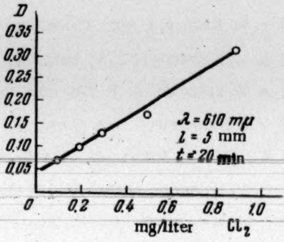


Fig. 8. Calibration curve for the determination of chlorine concentrations in water by a chloroform-extraction variant of the indophenol reaction.

Following the order in which solutions should be added to each other, as indicated above, a calibration curve was drawn which, for the purpose of comparison, is shown on Fig. 4; by means of this, it is possible to determine 5-100 γ/ ml Cl_2. Measurements were made at 610 mμ, 10 minutes after pouring the solutions together, using a cuvette with l = 5 mm; distilled water was used as reference standard.

In order to increase the sensitivity of the method down to 0.1 γ/ ml Cl_2, i.e. to the sensitivity of the o-toluidine reaction, a chloroform-extraction technique was worked out.

To 200 ml of test water in a 300 ml separating funnel was added 30 ml chloroform, and the mixture acidified with two drops of 5 N hydrochloric acid. Funnel and contents were shaken 5-6 times. The chloroform layer was run off into another separating funnel (50 ml capacity) and then 3 ml of 1 N NaOH added. Chlorine was extracted by shaking for one minute. To the sodium hydroxide solution, after removing it from the chloroform, was added 0.1 g of phenol and 1 drop of aniline. The intensity of the blue or light blue (depending on the chlorine concentration) color was measured after 20 minutes on a photometer at 610mμ using a cell with l = 5 mm. The calibration curve used for chlorine determination by this variant is shown on Fig. 8.

Within the concentration range studied, the solutions obey the Lambert-Beer law.

On the basis of the determination of chlorine in the presence of bromine, iodine, and other oxidizing agents as an example, it is clear that by making the correct choice of synthetic reaction, and by ensuring that it is carried out under the right conditions, there is a real possibility of determining materials which resemble each other closely with respect to their chemical properties.

In conclusion, it should be emphasized that when use is made of synthetic reactions, a study of their mechanism is of special interest.

SUMMARY

1. The nitrophenol reaction is strictly specific for Cl_2; such oxidizing agents as bromine, iodine, trivalent manganese salts, trivalent iron, hydrogen peroxide, and mono- and dichloramines, have no appreciable effect on the reaction. A method which has been developed for determination of chlorine, using this reaction as a basis, permits down to 0.1 γ/ ml of Cl_2 to be determined, and can be used instead of the o-toluidine method.

2. The mechanism of the reaction which occurs under the influence of chlorine, between aromatic amines phenols in alkaline media, has been studied.

LITERATURE CITED

[1] L. M. Kulberg, Organic Reagents in Analytical Chemistry (State Chem. Press, Moscow - Leningrad, 1950).

[2] L. M. Kulberg, J. Appl. Chem. 10, 1130 (1937).

[3] L. M. Kulberg and Z. V. Ivanova, J. Anal. Chem. 2, 43 (1947).

[4] A. K. Babko and A. T. Pilipenko, Colorimetric Analysis (State. Chem. Press, Moscow, 1951).

[5] V. I. Kuznetsov, J. Gen. Chem. 14, 897 (1944).

[6] R. F. Milton, Nature 164,No. 4167, 448 (1949).

[7] C. U. Houghton, Analyst 75, 180 (1950).

[8] J. Nusbaum and R. Skupeko, Anal. Chem. 23, 1881 (1951).

[9] A. Villiers and M. Tayolle,Compt.rend. 118, 1152 (1894).

[10] E. Hintz and H. Weber, Z. anal. Chem. 34, 599 (1895).

[11] M. C. Denige, Bull. soc. chim.(3 ser.) 5, 66 (1891).

[12] F. Raschig-Ludwigshafen, Z. angew. Chem. 20, 2065 (1907).

[13] Reactions and Reagents for the Qualitative Analysis of Inorganic Compounds (State Chem. Press, Moscow - Leningrad, 1950), p. 216.

[14] N. N. Voroshtsov, Bases of the Syntheses of Intermediate Products and Dyes (State Chem. Press, Moscow - Leningrad, 1950), p. 652.

[15] G. Mikhailov, Trans. Inst. Chemical Reagents 1939, No. 17, 45.

[16] S. I. Burmistrov and I. A. Titov, J. Gen. Chem. 22, 999 (1952) (T.p. 1053). *

[17] I. Kolthoff, Pharm. Weekblad. 69, 1147 (1932); Chem. Zentr. 1932, II, 3752.

Received February 8, 1955

---

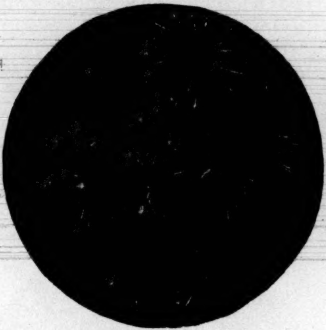
* T.p. = C. B. Translation pagination.

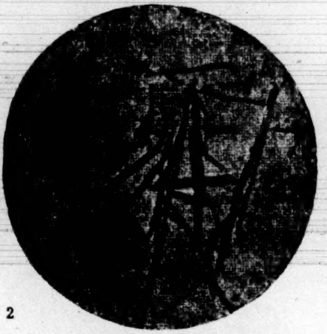
MICROCRYSTALLOSCOPIC IDENTIFICATION OF BARBITURATES

L. I. Rapaport

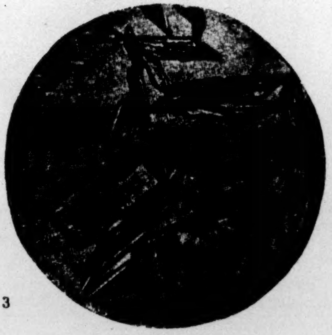
Central Scientific Research Drug Laboratory(TsNIAL) of the Chief Administration of Dispensaries of
the Ukrainian SSR Ministry of Public Health

Some papers have already been devoted to crystalloscopic identification of barbiturates [1-3]. We have developed the following simple method of preparing characteristic crystals of consistent shape for various barbituric acid derivatives. A drop of a hot 1% aqueous solution of the acid form of the barbiturate (a 3% solution in the case of Veronal) is placed on the object glass; when this is done crystals of consistent shape are immediately precipitated which are examined under a microscope.

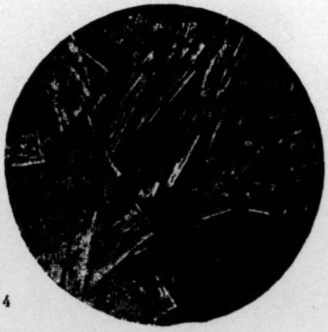




2

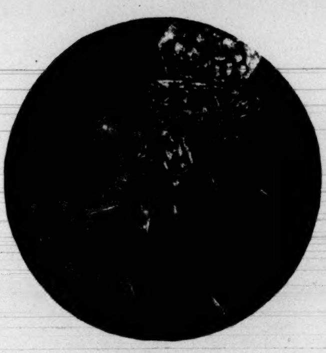


3

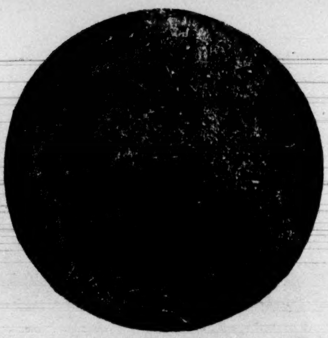


4

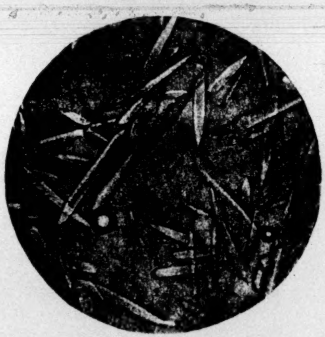
Fig. 1. Luminal × 200. Radial clusters of needle-like crystals.
Fig. 2. Luminal-Sodium × 110. Needle-like crystals and stars.
Fig. 3. Veronal × 110. Tablet-like aggregates of crystals.
Fig. 4. Medinal × 220. Prismatic, monoclinic oblique prisms.



5



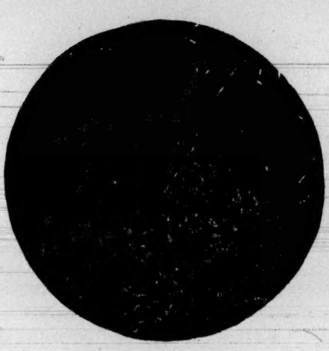
6



7

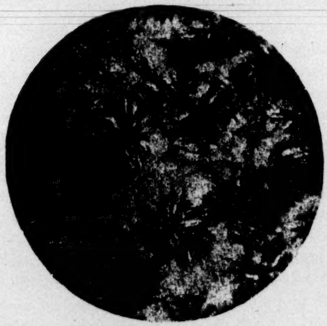
8

Fig. 5. Malyl (Dial)× 110. Prismatic hexagonal crystals.
Fig. 6. Rectone (Acid) × 110. Rod-like crystals.
Fig. 7. Quietal (Noctal) × 110. Hexagonal elongated crystals.
Fig. 8. Thiopental - Sodium (Pentothalsodium) × 320. Star-like crystals.

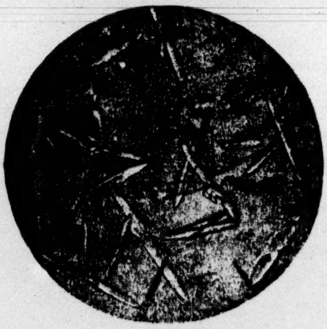


9

10



11



12

Fig. 9. Barbamyl (Amytal - Sodium) × 110. Dendritic crystals.

Fig. 10. Ethaminylsodium (Nembutal, Pentobarbityl - Sodium) × 110. Rod-like crystals, drawn out at the center.

Fig. 11. Hexanal (Evipan-Sodium) × 110. Radial ray-like dentritic crystals.

Fig. 12. Phanodorm × 110. Hexagonal elongated crystals, wider at the middle.

When studying the sodium salts of barbiturates, a small drop of 3-5% aqueous solution of barbiturate is placed on the object glass, covered with a cover slip; a drop of dilute sulfuric acid is then placed at the edge of the cover slip so that it can penetrate underneath the latter. Crystals which are characteristic for the given barbiturate are then formed (see micro-photographs).

The crystalloscopic method of detecting barbiturates is of particular importance for distinguishing barbiturates from each other. The crystalloscopic method is the only reliable method for identification of isomers of Amytal - Sodium (Barbamyl), and Ethaminal - Sodium (Nembutal), and also for the group of Bromalyl barbiturates.

Received December 13, 1954

LITERATURE CITED

[1] M. M. Pesez, J. pharm. chim. 28, 69 (1938).

[2] E. Rozhdestvenskaya, Pharmacy 4, 1 (1938).

[3] A. I. Kostyakova, Pharmacy 5, 37 (1942).

A NOMOGRAM FOR CALCULATING THE WEIGHT OF SAMPLE TO TAKE FOR DETERMINING MOLECULAR WEIGHT CRYOSCOPICALLY

N. B. Kondukov

Moscow Institute of Chemical Machine Construction

The accuracy of the cryoscopic method of determining molecular weight depends to a large extent on the concentration of test material in the original solvent [1]. The true molecular weight of a material (within the limits of experimental accuracy of the method), taking into account its concentration in the solvent can be calculated by two methods: 1) extrapolation of results obtained experimentally for the molecular weight to zero concentration; and 2) by carrying out determinations with concentrations of test material in the solvent, such that experimental errors in determining the molecular weight arising as a result of the concentration of test material do not exceed the accuracy of the method itself (i.e. an error of $< 5\%$). In laboratory practice the second method is often used, since it does not require a large number of replicate determinations of the molecular weight and is convenient for series analyses. All the same, when this method is used, it is necessary to use fairly accurately weighed amounts of test material, because of the necessity of working within a narrow concentration range, all the more so when as is usually the case, one lot of solvent is used for determining the molecular weight. It is particularly important to use accurately weighed amounts when using small amounts of solvent [2].

A nomogram is suggested for rapid calculation of weight of sample to take. A nomogram is convenient to use for series determinations of molecular weights, and for replicate analysis in one lot of solvent. In order to construct a nomogram it is necessary to know the limits of permissible concentration of test material in various solvents. In the theory of cryoscopy, concentrations are given in molar parts (mols of material/ 1000 g of solvent) [3,4]. In published information on cryoscopy concentration limits are given frequently in grams of material per 100 g;[5-7], or in parts by weight [8-9].

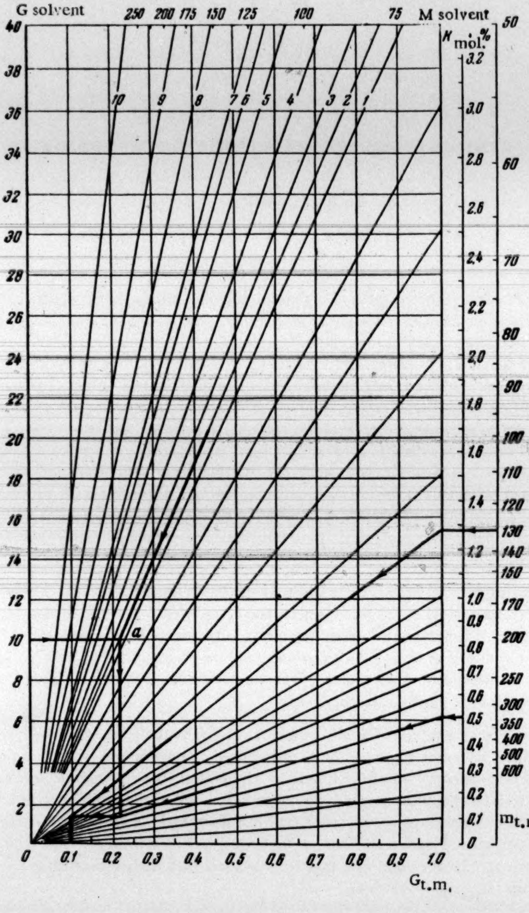
An examination and an analysis of published experimental work on the cryoscopic method of determining molecular weights [1-9], indicates a wide limit of permissible concentrations when using a method where no correction is applied for concentration of the solution. The permissible concentration limits depend on the properties of test material and solvent respectively (association and dissociation of materials, solvation in solution, heat of fusion of solvent, molecular weight of test material). Variations in concentration of the solutions used in the papers quoted were as follows: 1-9.5% weight; 0.3-3.2% mol; 0.04-0.45 molal parts. Within this range are included permissible concentrations for materials with molecular weights $M_{\text{test material}} = 60$-600, in various solvents ($M_{\text{solvent}} = 18$-284).

The aim of the nomogram is a fairly accurate and rapid determination of the weight of test material $G_{t.m.}$ in g, to be dissolved in the given amount of solvent G_{solvent}. According to the concept of molar parts we then get:

$$\frac{G_{t.m.}}{M_{t.m.}} : \left(\frac{G_{t.m.}}{M_{t.m.}} + \frac{G_{\text{solvent}}}{M_{\text{solvent}}} \right) = \frac{k}{100},$$

where k is the molar %.

Since $\frac{G_{t.m.}}{M_{t.m.}} << \frac{G_{\text{solvent}}}{M_{\text{solvent}}}$ then it is possible, with sufficient accuracy for the nomogram, to put



$$\frac{G_{t.m.}}{M_{t.m.}} : \frac{G_{solvent}}{M_{solvent}} = \frac{k}{100}$$

or

$$\frac{G_{t.m.}}{M_{t.m.}} = \frac{k}{100} \cdot \frac{G_{solvent}}{M_{solvent}} \,. \qquad (1)$$

A radial nomogram is constructed with the aid of Equation (1), the limits of the values of which along the axes are given in the diagram. Along the $M_{solvent}$ axis of the nomogram is plotted in round figures the molecular weight of solvent, while in the plane of the nomogram are given ten rays 1-10 for certain solvents: 1) ethyl ether and tertiary butyl alcohol ($M_{solvent} = 74.12$); 2) benzene ($M_{solvent} = 78.11$); 3) cyclohexane ($M_{solvent} = 84.16$); 4) phenol ($M_{solvent} = 94.11$); 5) toluidine ($M_{solvent} = 107.15$); 6) indene ($M_{solvent} = 116.15$); 7) nitrobenzene ($M_{solvent} = 123.11$); 8) camphor ($M_{solvent} = 152.23$); 9) ethylene bromide ($M_{solvent} = 187.88$); 10) stearic acid ($M_{solvent} = 284.47$). For determination of molecular weights using small amounts of solvent and test material, the nomogram should be reconstructed with condensed scales of $G_{solvent}$ and $G_{t.m.}$: for this purpose it is good enough to set new limits for $G_{solvent}$ and $G_{t.m.}$ with proportional decreases in their values (e.g. $G_{solvent} = 0 - 20$ g; $G_{t.m.} = 0 - 0.5$ g); the remaining values on the nomogram can then be left unchanged. For practical purposes a value of $k = 0.5 - 1.2\%$ mol for $M_{t.m.} << 400$ can be accepted as a fairly reliable value of the concentration for most of the commonly used solvents.

An example of the use of the nomogram. Determination of the molecular weight of a naphthalene fraction (expected to be roughly $M = 130$) was carried out in benzene (Ray 2) using $G_{solvent} = 10$ g of the latter. Three determinations were made in which the concentrations were k = 0.5, 0.7, and 1.0 mol respectively. For the first determination according to $G_{solvent} = 10$ g, and Ray 2 we get: "a", from which we produce the vertical to the intersection with the concentration ray $k = 0.5\%$ mol, and from this point draw a horizontal line to intersect the ray $M_{t.m.} = 130$. From this last point a vertical line is drawn to the $G_{t.m.}$ axis, from which we get the weight of material that should be used is $G_{t.m.} = 0.085$ g. The second determination was carried out in the same way, taking into account the more accurate molecular weight already established on the basis of the first determination. If for example, the molecular weight as determined in the first test was found to be $M_{t.m.} = 140$, then in the second run, one should proceed along the vertical downwards to the ray $k = 0.7\%$, and from the point of intersection thus obtained draw a horizontal to meet the ray $M_{t.m.} = 140$. In the second instance we get the weight that should be added $G_{t.m.} = 0.120$ g; i.e. one should add a weight of $0.120 - 0.085 = 0.035$ g more of test material to the original solvent with $G_{solvent} = 10$ g, containing $G_{t.m.} = 0.085$ g. of test material.

SUMMARY

1. A nomogram is given for calculating the weight of material to take during cryoscopic determination of molecular weights.

2. The nomogram is convenient for series analyses and for replicate determination of molecular weight in one lot of solvent.

Received November 22, 1954

LITERATURE CITED

[1] K. S. Ramaiya and K. A. Shegrova, Factory Lab. 8, 404-408 (1939).

[2] V. Ya. Mikhelson. J. Anal. Chem. 9, 22-28 (1954)(T.p. 21).*

[3] K. Weygand, Experimental Methods in Organic Chemistry (Foreign Lit. Press, Moscow, 1951), Part III, pp. 134-137.

[4] A. Weissberger, Physical Methods in Organic Chemistry (Foreign Lit. Press, Moscow, 1950), I, p. 48.

[5] E. Beckmann, Z. physik. Chem. 7, 323-330 (1891); 21, 239-257 (1896).

[6] A. N. Sakhanov and N. A. Vasilev, Petroleum Economy 14, 643-650 (1928).

[7] B. Kaminer, Petroleum Economy 11, 219-223 (1926).

[8] B. M. Rybak, Analysis of Petroleum and Petroleum Products (State All-Union Trust of the Azerbaidzhan Oil and Gas Industry Press, 1948), Part I, p. 69-75.

[9] N. Khazhak, Azerbaidzhan Petroleum Economy 18, 76-80 (1938).

---

* T.p. = C. B. Translation pagination.

BLANK
PAGE

DETERMINATION OF THE DEGREE OF BRANCHING OF $C_{12} - C_{16}$ PARAFFIN HYDROCARBONS BY INFRA-RED SPECTROSCOPY

Yu. P. Egorov and Al. A. Petrov

Institute of Organic Chemistry, Acad. Sci. USSR, Moscow

The practical requirements of industry for special fuels containing high molecular weight alkanes, makes it necessary to search for a method of analyzing the molecular composition of individual fractions of this fuel. In the present article we have attempted to solve this problem by using the method of relative evaluation of the intensity of infra-red absorption bands in the region of valency CH-vibrations (3.5-3.35 μ).

1. The Region of CH- Vibrations in Branched Alkanes

Wide lines (bands) with maxima located approximately at 2856, 2875, 2905, 2936, 2965 cm^{-1} (3.50; 3.48; 3.44; 3.42 and 3.38 μ respectively) are always observed in the combined scattering spectra and infra-red absorption spectra of alkanes. The group characteristics of these frequencies is, at present, rather a contradictory question. The group characteristics of CH-vibrations, according to our results [1], are given in Table 1 (line 1). CH_3 groups which are indicated in the second line of Table 1 do not determine the basic intensity of the bands of high molecular weight alkanes, but are superimposed on it, thereby distorting the proportionality between the number of groups and band intensity. The appearance of these fundamental frequencies, can apparently be explained by splitting of basic frequencies thanks to intermolecular reactions.

TABLE 1
Group Characteristics of Frequencies in the CH-Vibration Region

Frequency in cm^{-1}				
2856	2875	2905	2936	2965
CH_2	CH, CH_3	CH_2, CH_3	CH_2	CH_3
CH_3	CH_3	—	CH_3	—

The group relation, given in line 1, allows one to expect a growth in the intensity of the infra-red band 3.38 μ (2965 cm^{-1}) with the number of CH_3 groups, i.e. with branching of the alkane. Actually, it is clear from a consideration of Fig. 1, on which is represented the infra-red spectra of several alkanes of composition C_{12} that there is a decrease in peak intensity at 3.50 and 3.42 μ with decreasing number of CH_2 groups, and of an increase in peak 3.38 with with increasing number of CH_3 groups. The increase in the peak at 3.48 μ with branching in the test paraffin, can be explained either by the increase in number of CH_3 groups, as in the case of Sushchinsky [3], or as a result of an increase in the number of CH groups, as indicated in Table 1. In order to get a more accurate picture, let us consider Fig. 2 on which is represented the infra-red spectra of 2,3,4, 5-tetramethylhexane and 2,2,4,6, 6,-pentamethylheptane. Despite the large number of CH_3 groups, the 3.48 μ peak in the latter alkane has a small intensity, while in the first alkane it is sharply defined. This result also permits one to regard the 3.48 μ peak as the result of the frequency of the CH group on the tertiary carbon atom. The weakness of the 3.45 μ (2900 cm^{-1}) peak in all alkanes, as well as in 2,2,4,6, 6-pentamethylheptane is of special interest. This frequency, probably, relates to symmetrical vibration in the CH_3 group and only increases its intensity significantly in the presence of CH_3 groups which are connected to the quaternary carbon atom.

Thus, the characteristic changes in the spectra (Figs. 1 and 2), which were observed for alkanes of any composition, permits one to make a qualitative distinction in the degree of branching of methylated carbon chains.

On comparing alkanes with equal amount of branching, but different composition, it is possible to detect their qualitative unity. On Fig. 3 are given the infra-red curves for alkanes of normal structure C_{12}, C_{14}, C_{16} and of mono-substituted ones: 2-methylundecane, 2-methyltridecane, and 6-methylpentadecane. A common qualitative agreement can be observed between all the spectra which have clearly defined peaks at 3.51 and 3.42 μ and a weaker peak 3.38 μ. At the same time one can see a more clearly defined peak at 3.42 in C_{12} against, e.g. C_{16}, with respect to the neighboring band at 3.38 μ. This fact agrees with expectations, since in the case of long carbon chains (C_{16}) the ratio of the frequency of the CH_3 group to the CH_2 groups is less than in the short carbon chains (C_{12}).

On comparing the infra-red spectra of alkanes of similar composition but in which the substitutent groups (CH_3 groups) are located in different positions, one can see that they agree closely together (Fig. 4). This fact, to an appreciable extent, restricts the possibility of analysis; nevertheless, it allows one to evaluate the mean branching of multi-component fractions.

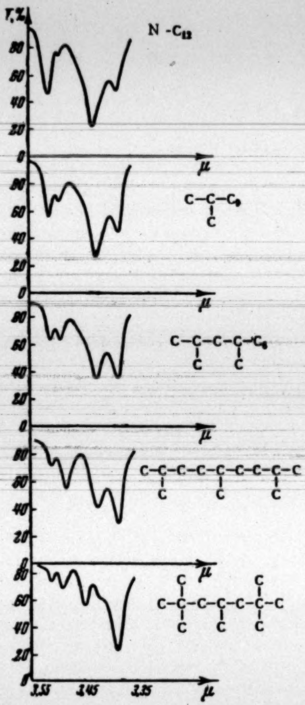


Fig. 1. Infra-red spectra of alkanes C_{12} in the 3.35 - 3.55 μ region.

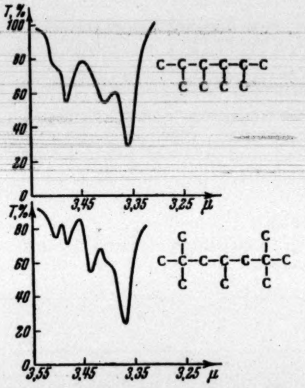


Fig. 2. Infra-red spectra of alkanes with ternary and quaternary carbon atoms.

2. Experimental

In order to get clearly defined absorption bands in the CH- vibration region we used CCl_4 solutions of the test alkane, since this solvent does not have any absorption bands in this region. The concentration of test alkane used was 2% by volume. We used a rock salt cell, thickness 0.12 mm. The thickness of the layer was ensured by the construction of the cell itself, in which the central part of one of the plates was worn down to the indicated depth and surrounded by a groove for collecting any excess material. Spectra were obtained on an IKS-11 spectrometer, using an LiF prism with constant values of the entry and exit slits of 0.2 mm, and standard burning conditions – 0.65 A and a voltage of 2.0 V on the FEOU amplifier. The time taken to register one spectrum in the 3.6-3.3 μ region was 8 minutes. Intensity was determined by measuring the galvanometer deviations for the minimum of the band (I) and the background (I_0) – the spectrum of pure CCl_4 in the same region.

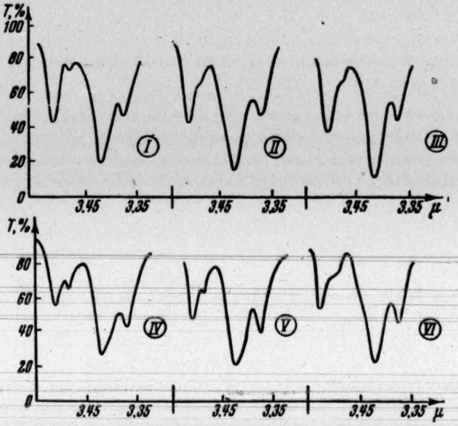


Fig. 3. Infra-red spectra of n- and mono-substituted alkanes [I) n-C_{12}; II) C_{14}; III) n-C_{16}; IV) 2-methylundecane; V) 2-methyltridecane; VI) 6-methylpentadecane].

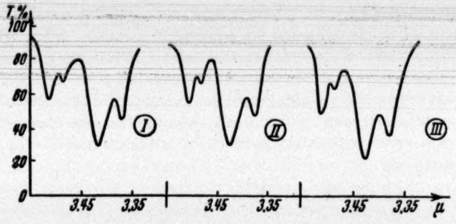


Fig. 4. Infra-red spectra of mono-substituted C_{12} alkanes in which the CH_3 groups are located in different positions: CH_3 I) 2; II) 3; III) 5-methylundecane.

3. Method of Evaluating the Degree of Branching

Since the intensity of the infra-red bands (at the maximum) can be determined for alkanes on the basis of a known relation, from the Lambert - Beer law logarithm $\frac{I_0}{I}$ = Kcd, where c is the concentration; d, the thickness of the layer; K, absorption coefficient, one would expect a proportionality between the growth of optical density (logarithm $\frac{I_0}{I}$) or K, with the number of similar type groups (CH_3, CH_2, CH), since this number enters into "c". This increase is confirmed, to a considerable degree, by the results given above in Figs. 1 and 2. At the same time, thanks to the differences in the group characteristics of each band (Table 1) and the nearness of the bands themselves to each other, this increase is not a sufficiently simple function of the number of groups considered. Hastings et al.[2], occupied with a similar problem to ours, suggested taking into account the share of each band in the total absorption K, by using a relation of the type $K = aN_{CH_3} + bN_{CH_2}$, where a and b are certain coefficients, determined from mean experimental values, and from this determine the number (N) of CH_2 and CH_3 groups on the basis of measurements of the absolute value of the absorption coefficients of two bands, e.g. 3.42 and 3.38 μ, the group characteristic of which coincided with ours. The authors quoted got satisfactory results for C_5 - C_8 hydrocarbons, but got appreciable errors in determining the number of groups for C_{12} alkanes and higher (e.g. according to the results of the authors themselves, n-dodecane contains no CH_3 groups, while hexadecane contains 2).

We evaluate the degree of branching graphically: by measuring the ratios of the intensity of the bands 3.42 and 3.51 μ to 3.38 μ. Since, as can be seen from Fig. 1, the intensity of the first two bands will decrease with branching, while the intensity of the latter band increases, their relative intensity will be a very sensitive value; it will not depend directly on concentration and layer thickness. Actually, if

$$\log \int \left(\frac{I_0}{I}\right)_{3.38\mu} = K_1cd \text{ and}$$

$$\log \left(\frac{I_0}{I}\right)_{3.42\mu} = K_2cd, \text{ then } a = \frac{\log\left(\frac{I_0}{I}\right)_{3.42}}{\log\left(\frac{I_0}{I}\right)_{3.38}} = \frac{K_2}{K_1},$$

similarily, $b = \frac{K_3}{K_1}$, where K_3 relates to the 3.51 μ band. Using the method just described, we constructed graphical relationships of a and b as a function of the number of CH_2 groups on the basis of measurements of the infrared spectra of 28 different alkanes which we had specially synthesized — C_{12} — C_{16}*, viz: n-dodecane; 2-, 3-, 5-, 6-methylundecanes; 2,3-, 2,4-, 2,5-dimethyldecanes; 2,5,8-trimethylnonane; 2,2,4,6,6-pentamethylheptane; n-tridecane; 2-, 3-, 4-, 6-methyldodecanes; 2,4-dimethylundecane; n-tetradecane; 2-, 3-, 4-, 6-methyldodecanes; 2,4-dimethylundecane; n-tetradecane; 2-, 4-, 6-, 7-methyltridecanes; 2,4-dimethyldodecane; n-pentadecane; 4-methyltetradecane; 2,4-dimethyltridecane; n-hexadecane; 6-methylpentadecane; 2,4-dimethyltetradecane, and 2,3,4,5-tetramethylhexane. Results of these measurements are given on Figs. 5 and 6. As is evident from Figs. 5 and 6, experimental points are arranged in a definite order. Thus, if one connects the mean points of alkanes of the same composition with different degrees of branching, the lines obtained are displaced parallel to one another, which appears to be a certain characteristic of the alkane of each composition. Lines connecting points of equal degree of branching (equal number of CH_3 groups, given by dotted lines), are displaced in parallel, and decrease with increasing number of CH_3 groups in the side chain. Between the dotted lines there is an appreciable difference, which also allows one to determine numerically the number of CH_3 and CH_2 groups in the branched paraffins.

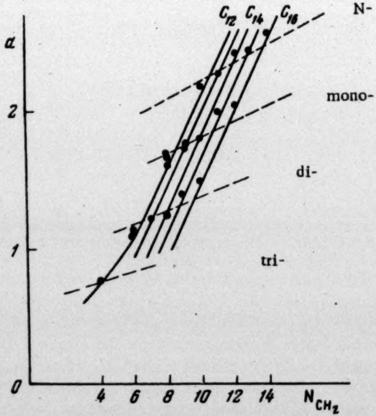


Fig. 5. Relation between the ratio $\frac{I_{3.42}}{I_{3.38}}$ and the number of CH_2 groups in alkanes.

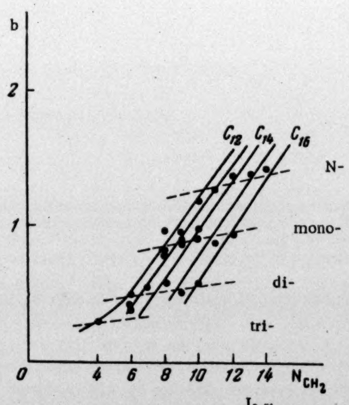


Fig. 6. Relation between the ratio $\frac{I_{3.51}}{I_{3.38}}$ and the number of CH_2 groups in alkanes.

---

* The syntheses and properties of these compounds will be described in a special paper.

Thus, a comparison of experimental infra-red curves, obtained by means of the method suggested, with Fig. 1, and an evaluation of the ratios a and b, on using the graphs on Figs. 5 and 6, permits one to make a semi-quantitative estimation of the degree of branching of the alkane studied.

It is essential to clarify the quantitative side of such measurements when applied to mixtures.

As pointed out already, the very essence of the method suggested means that one only evaluates the mean property for a given mixture, since one can have isomers with equal numbers of CH_3 groups which are however located in different parts of the chain. In order to determine the scope and the limits of the method we made up several synthetic mixtures and took their infra-red spectra; the hydrocarbons used were dodecanes with differing degrees of branching. Results of measurements are compared with the theoretical number of CH_3 groups, in Table 2.

TABLE 2
Accuracy of Determination of the Composition of Mixtures

Composition of mixture	Number of CH_3 groups			Error in %
	Using a	Using b	Theoretical	
50% normal and 50% mono-substituted	9.0	8.5	9.0	3
ditto, but 75 and 25%	9.1	8.5	9.5	7
ditto, but 25 and 75%	8.75	8.0	8.5	4
75% mono- and 25% disubstituted	7.8	7.9	7.5	5
ditto, 25 and 75%	6.5	7.0	6.5	4

Thus, the accuracy obtained for determining the composition of mixtures is ~ 10% when relation a is used.

In conclusion, it is necessary to make some observations on the practical use of the graphs given in Figs. 5 and 6. Undoubtedly, the value of the ratios a and b depend essentially on the apparatus used (resolving power, recording sensitivity, etc.), since superposition of neighboring strips always occurs, e.g. 3.38 and 3.42 μ. Accordingly, the practical qualitative character of the infra-red spectra will be the same as shown in Figs. 1-3, but with quantitative differences in the ratios a and b. There are grounds for assuming that the values of a and b will differ from our results by some constant coefficient, determination of which can be carried out by measuring several standard hydrocarbons, and the ratios of a and b compared with Figs. 5 and 6.

SUMMARY

On the basis of accurate group relations of the frequencies of the valency vibrations of CH groups, a method is suggested for evaluating the degree of branching of C_{12} - C_{16} alkanes on the basis of their infra-red absorption spectra.

Received June 20, 1955

LITERATURE CITED

[1] Yu. P. Egorov, Bull. Acad. Sci. USSR, Phys. Section 1954, No. 6, 702.

[2] S. Hastings et. al., Anal. Chem. 24, 612 (1952).

[3] M. M. Sushchinsky, Bull. Acad. Sci. USSR, Phys. Section 1947, 11, 341.

BLANK
PAGE

COLORIMETRIC DETERMINATION OF SULFIDE IONS BY THE MOLYBDENUM-THIOCYANATE REACTION

V. A. Nazarenko and M. B. Shustova

In a recently published article by Koren and Gierlinger [1], color reactions for the sulfide ion were discussed from the point of view of making use of them for colorimetric analysis. After a study of the formation of the molybdenum-thiocyanate complex during reduction with sulfide [2], the authors concluded that this reaction is unsuitable for quantitative measurements on account of the instability of the colors of the solutions. This conclusion is however only true with respect to the reagent which these authors used, which was obviously not suitable for quantitative work. Tests showed that the molybdenum-thiocyanate reaction can serve as a basis for a fairly sensitive colorimetric method of determining sulfide ions, if one takes into account the properties of the molybdenum-thiocyanate complex.

Pepkowitz and Shirley's reagent [2], is a mixture of aqueous hydrochloric acid solutions of ammonium molybdate and potassium thiocyanate, which has a yellow color. On addition of sulfides, a red color develops as the result of formation of the molybdenum-thiocyanate complex. The color is very unstable and at low sulfide concentrations (0.5 - 1γ S^{2-})becomes indistinguishable from the color of a blank after only one minute.

The instability of the color of aqueous solutions of the molybdenum-thiocyanate complex has been known for a long time, and, accordingly, it has been recommended that for accurate determination of molybdenum by the thiocyanate method,particularly for the determination of small amounts of molybdenum, the complex be extracted with an organic solvent [3]. The study of molybdenum-thiocyanate complexes in solution which was carried out by Babko [4], explains why the color of these solutions is so unstable. It follows from Babko's work that as a result of step-like dissociation in aqueous solutions, several compounds of Mo^V and CNS^- may be formed; first of all a compound is formed with a ratio of Mo:CNS of 1:5; it is the formation of this compound which is the basis of the colorimetric method. Even if one excludes the possibility of a further reduction of quinquevalent molybdenum by excess reducing agent, there is still formation of a compound with a lower ratio of CNS^- to Mo and a smaller molar extinction coefficient, as the result of dissociation on standing, and expulsion of thiocyanate ions from the inner sphere of the complex. The idea of extracting the complex into the organic solvent is to prevent dissociation of the complex, and formation of compounds which are poorer in thiocyanate.

One of us, in conjunction with Poluetkov [5], long ago pointed out that addition of an organic solvent, which is miscible with water, in particular ethyl alcohol, to a solution of the molybdenum-thiocyanate complex also stabilizes the color by suppressing dissociation of the complex. Acetone behaves similarily to alcohol [6]. On Fig. 1 is shown the results of measurements with time, of the absorption curves of aqueous and aqueous-alcohol solutions respectively of the molybdenum-thiocyanate complex, obtained by reduction with stannous chloride.

The following solutions were used for the measurements:

1) 2 ml of a neutral solution of potassium molybdate in 3% potassium chloride (200 γ Mo), 5 ml of 25% potassium thiocyanate, 2.5 ml of a 5% solution of stannous chloride in hydrochloric acid (1:1), and water to bring the volume up to 50 ml.

2) 2 ml of a solution of potassium molybdate in 3% potassium chloride, 5 ml of 25% potassium thiocyanate, 25 ml of 96% athyl alcohol, 2.5 ml of 5% stannous chloride, and the volume made up to 50 ml with water.

Measurements were made in a photometer in a 20 mm cell against water as the blank.

As can be seen from Fig. 1, for the aqueous solution, the absorption at the maximum 470 mμ and 430 mμ falls rapidly with time, but changes little at other wave lengths. Visually this is manifested by a change in the shade of the color, in addition to a general weakening. At the same time the absorption curve for aqueous-alcohol solution remains unchanged during the whole of the observation time (2 hours).

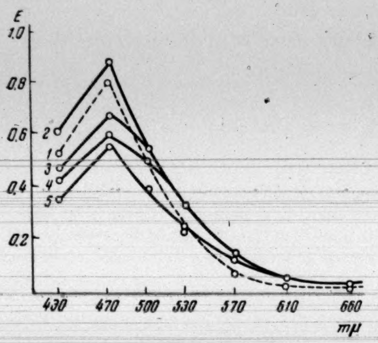


Fig. 1. Effect of alcohol on color stability: 1) an aqueous-alcohol solution 5 minutes, and 2 hours after mixing; 2) an aqueous solution 0.5 minute after mixing; 3) ditto after 30 minutes; 4) ditto after 1 hour; 5) ditto 2 hours after mixing.

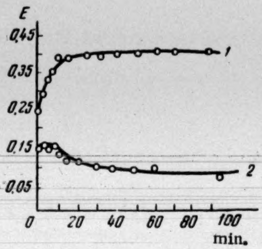


Fig. 2. Effect of alcohol during the molybdenum-thiocyanate reaction for sulfide: 1) in the presence of alcohol; 2) in the absence of alcohol.

A similar phenomenon is observed also during the action of sulfide on a mixture of hydrochloric acid solutions of ammonium molybdate and potassium thiocyanate, both containing, and free from, alcohol respectively. On Fig. 2 is shown the change in optical density of solutions with time in the absence and and in presence of alcohol. One solution consisted of 0.75 ml of 2.5% solution of ammonium molybdate in hydrochloric acid (1:10), and 0.75 ml of a 5% solution of potassium thiocyanate in hydrochloric acid (1:10), and 1 ml of 96% alcohol. To a freshly prepared mixture was added 0.5 ml of sodium sulfide (3.5 γ S^{2-}). The second solution consisted of 1.25 ml of ammonium molybdate solution and 1.25 ml potassium thiocyanate solution, prepared as indicated above. To this freshly prepared mixture was also added 0.5 ml of a fresh solution of sodium sulfide (3.5 γ S^{2-}). Measurements were carried out in a 10 mm cell at 470 mμ, using water as reference.

It is clear from Fig. 2 that while the optical density of an aqueous solution falls very rapidly in the first minutes after preparation, the optical density of an aqueous-alcohol solution rapidly increases, achieving a maximum after 10 minutes; after which it remains practically constant during all the time it is observed (1.5 hours).

The sensitivity of the reaction increases on using an aqueous-alcohol reagent, and permits determination of as little as 0.2 γ S^{2-} (as Na_2S).

The use of an aqueous-alcohol reagent also premits one to carry out colorimetric determinations. The relation between color intensity and the amount of sulfide sulfur, within the limits which we studied, 0.2 - 5γ S^{2-}, is linear, as can be seen from Fig. 3.

Solutions used for determining the relation between optical density and amount of sulfide sulfur, were prepared as described above. Measurements were made 20 minutes after mixing the solutions at a wave length of 470 mμ in a 10 mm cell, using water as a reference.

It is therefore clear from what has been said that an acid solution of ammonium molybdate and potassium thiocyanate can only be used as a reagent for sulfide ions when an organic solvent is added to it, which prevents dissociation of the molybdenum-thiocyanate complex formed. A hydrochloric aqueous-alcohol solution of ammonium molybdate and potassium thiocyanate can also be used for colorimetric determinations of microgram amounts of sulfide sulfur, naturally, in the absence of other reducing agents.

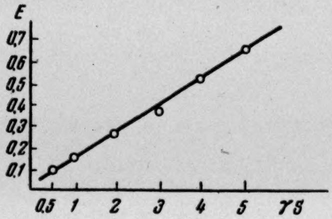


Fig. 3. Relation between color intensity and amount of sulfide

LITERATURE CITED

[1] H. Koren and W. Gierlinger. Microchemie ver.Mikrochim. Acta 3, 220 (1953).

[2] L. P. Pepkowitz and E. L. Shirley. Anal. Chem. 23, 1709 (1951).

[3] E. B. Sandell, Colorimetric Determination of Traces of Metals (State Chem. Press, 1949), p. 327.

[4] A. K. Babko, J. Gen. Chem. 17, 642 (1947).

[5] V. A. Nazarenko and N. S. Poluektov, Short Textbook on Qualitative and Quantitative Analysis of Ores and Minerals under Field Conditions (West Siberian Geol. Administration Press, Tomsk, 1943), p. 98.

[6] F. S. Trimaldi and R. C. Wells, Ind. Eng. Chem. Anal. Ed. 15, 315 (1943).

Received May 25, 1955

BLANK
PAGE

QUANTITATIVE DETERMINATION OF DICHLOROBENZENE ISOMERS

A. A. Spryskov and Yu. G. Erykalov

Ivanov Chemico-Technological Institute

During chlorination of benzene or chlorobenzene, the isomers predominantly formed are the ortho and para isomers; only a small amount of the meta isomer is formed. The first method used for the quantitative determination of dichlorobenzenes in their mixtures was the thermal method of Van der Linden [1], based on the fact that the ortho and meta isomers depress the setting temperature of a para isomer to a different extent till the para isomer content falls below 45%. By adding, if necessary, pure p-dichlorobenzene to mixtures, it is possible thereby to establish the content of the para isomer. The ratio of the ortho to the meta isomer is found by means of the second setting point after precipitation of the para isomer.

Zilberman and Gorlach [2], during a study of the polychlorides of a chlorobenzene factory, determined only the ortho and para isomers, leaving aside the question of the meta isomer, by distillation, and determining the setting temperature and the specific gravities of the fractions.

Japanese research workers [3], determined o- and p-dichlorobenzenes in binary mixtures by determining the dielectric constant by means of a resonance method with a high frequency oscillator. Here again the determination of the meta isomer has been left alone.

The only existing method whereby all three isomers can be determined, viz. Van der Linden's method, is however not always reliable, since the second setting point, as Van der Linden points out, is very difficult to determine, since it is found at too low a temperature. At the same time, in certain cases, so much solid phase separates out, that mixing becomes impossible.

In order to solve this problem of determining all three isomers, we used the thermal method for determining the para isomer, and then a bromide-bromate method for determining the meta isomer, after introducing an amino group into the nucleus. The bromide-bromate method has been used previously for determining the isomers of toluidine [4], xylidene [5], and other amines, and also of phenols and nitro compounds after reduction of the later with titanium trichloride [4].

EXPERIMENTAL

In order to determine the p-dichlorobenzene in mixtures, part of the setting curve for ternary mixture of the para, ortho, and meta isomers was studied. The results obtained, which are presented in Table 1, showed that a smooth curve can be obtained, which coincides almost entirely with the curves of the binary mixtures para-ortho and para-meta respectively.

After establishing the para isomer content by means of the setting point of the test mixture, the latter is nitrated and then reduced for determination of the meta isomer by bromination.

An aliquot of the test material (~ 1.5 g) was mixed with an equal amount of water, and 15 g of nitric acid sp.gr. 1.5 added dropwise in the course of 30 minutes with adequate cooling. After standing for half an hour the mixture was poured into 50 ml water, and the product obtained washed in a separating funnel til the wash water was neutral; the water used for washing was warmed when the product solidifies.

In a wide test tube fitted with a ground glass tube serving as a reflux air condenser, the nitro compound was mixed with 6 g of zinc dust, and 30-40 ml of hydrochloric acid sp.gr. 1.18 added carefully with cooling until the zinc dust completely dissolved on subsequent boiling on a grid. Reduction took about 1 hour. The hot solution was poured into 250-300 ml water, filtered into a 500 ml standard flask; 60 ml of hydrochloric acid sp.gr. 1.18 was then added, and the whole made up to the mark. 100 ml of this solution was then titrated with 0.1 N sodium nitrite using Tropeoline 00 as indicator [6]; this allows the total amount S of amine to be determined by means of the formula:

$$S = \frac{162 \cdot a}{10000},$$

where a is the number of ml of 0.1 N sodium nitrite solution used for titrating.

For bromination, 25 ml of the solution in the standard flask was measured out and 0.1 N bromide-bromate solution added until the solution acquired a clear-cut yellow color; the test tube was then stoppered with a ground glass stopper and left for 30 minutes. To determine excess bromide-bromate, 2 g potassium iodide was added and iodine titrated after 5 minutes with 0.1 N thiosulfate, using starch as indicator.

TABLE 1

Setting Temperatures of Mixtures of Ortho-, Meta-, and Para-Dichlorobenzenes

Isomer content in the mixture in %			Setting temperature of mixture in °C	Isomer content in the mixture in %			Setting temperature of mixture in °C
para	ortho	meta		para	ortho	meta	
83.0	0	17.0	43.8	66.8	22.7	10.5	33.8
80.8	9.6	9.6	42.5	64.6	35.4	0	32.1
80.3	13.3	6.4	42.0	41.8	31.2	27.0	13.5
71.1	17.7	11.2	36.6	41.0	29.2	29.8	12.8
70.1	29.9	0	36.4	33.7	44.6	21.7	4.8

Nitration and reduction when carried out as described give five isomeric dichloroanilines. The amines obtained from meta-dichlorobenzene, on nitration give mono-bromo derivatives, while those obtained from the ortho- and para-dichlorobenzenes give dibromo derivatives. From the amount of bromine used in the titration it is possible to calculate the content in g of the dichloroanilines formed from ortho- and para- dichlorobenzene by means of the formula:

$$S_2 = \frac{162 \cdot V}{20000} - S\frac{25}{100},$$

where V is the volume in ml of 0.1 N bromide-bromate solution used for titration: 25/100 is the ratio of the volume of brominated solution to the volume of the diazotized solution.

The amount of dichloroanilines in g formed from meta-dichlorobenzene is given by:

$$S_1 = S\frac{25}{100} - S_2$$

while the meta-dichlorobenzene content in the mixture in % is given by:

$$\frac{S_1 \cdot 100}{S} \cdot \frac{100}{25}.$$

Knowing the para-dichlorobenzene content from the setting point of the mixture one can calculate the ortho-dichlorobenzene content by difference.

The method described was checked on synthetic mixtures made from the pure isomers of dichlorobenzene. The results, given in Table 2, show that the experimental error in determining each isomer is less than 1% of the total isomers.

This work therefore shows that the bromometric method which has been used before for determination of

TABLE 2

Checking the Method on Synthetic Mixtures

% of dichlorobenzene isomer taken			% of dichlorobenzene isomer found			Experimental error in %		
ortho	para	meta	ortho	para	meta	ortho	para	meta
100	0	0	99.8	—	—	—0.2	—	—
—	100	0	—	99.9	—	—	—0.1	—
0	0	100	—	—	99.4	—	—	—0.6
0	96.4	3.6	0	96.4	4.3	0	0	+0.7
0	93.3	6.7	0	93.4	6.6	0	+0.1	—0.1
35.4	64.6	0	35.4	64.3	0.3	0	—0.3	+0.3
28.9	71.1	0	28.4	70.9	0.7	—0.5	—0.2	+0.7
9.6	80.8	9.6	10.0	80.9	9.1	+0.4	+0.1	—0.5
9.7	84.9	5.4	10.2	84.9	4.9	+0.5	0	—0.5
29.2	41.0	29.8	29.2	41.0	29.8	0	0	0

the meta-isomer in mixtures of the isomers of amines, certain nitro compounds and phenols of the benzene series, can also be used for compounds not containing amino, nitro, or hydroxy groups.

This method may be used e.g. for determining the isomers of dibromobenzene and other substituted products which are readily nitrated and reduced like dichlorobenzene.

For this work the following materials were used: para-dichlorobenzene with a melting point of 53°; meta-dichlorobenzene prepared from pure meta-nitroaniline, via a Sandmeyer reaction, with a setting point of -25°; ortho-dichlorobenzene prepared from ortho-chloroaniline with setting point of -17.8°.

SUMMARY

A method has been worked out for determining meta-dichlorobenzene in a mixture of the three dichlorobenzene isomers; it is based on nitration, reduction, and bromination of the mixutre. In conjunction with the thermal method for determining the para isomer, this method permits one to determine the ortho isomer by difference. The error in determining the individual isomers is less than 1%. An analysis takes 5 -6 hours.

Received May 26, 1955

LITERATURE CITED

[1] T. Van der Linden, Rec. trav. chim. 30, 305 (1911).

[2] G. B. Zilberman and G. Ya. Gorlach, Aniline Dye Ind. 5, 385 (1935).

[3] T. Takahashi, K. Kimoto and T. Yamada, J..Chem. Soc. Japan, Ind. Chem. Sect. 54, 427 (1951).

[4] A. W. Francis and A. J. Hill. J. Am. Chem. Soc. 46, 2498 (1924).

[5] B. P. Fedorov and A. A. Spryskov, Ind. Org. Chem. 2, 101 (1936).

[6] A. E. Porai-Koshits and L. V. Chervinskaya, Aniline Dye Ind. 3, 399 (1933).

BLANK
PAGE

THE COMPOSITION OF URANYL SELENITE.

A VOLUMETRIC METHOD OF DETERMINING URANIUM

M. K. Djoshi

Benares University, India

Published information on the composition of uranyl selenite, and its use for quantitative determination of uranium, is very meager, despite the fact that attempts to make use of it were made a long time ago [1].

Preliminary experiments carried out in the laboratory at Benares University showed that a yellowish white precipitate of uranyl selenite is formed on addition of an aqueous solution of selenious acid to a solution of a uranyl salt at a pH of 4-5. The work described here was carried out in order to find out what are the factors that affect quantitative precipitation of uranyl selenite of a certain composition with the aim of developing a volumetric method of determining uranium.

The stock solution of uranyl sulfate was prepared by dissolving a Merck preparation of high purity in water. Uranium content was determined by the classical hydroxyquinoline method. Selenious acid recrystallized from absolute alcohol was used for preparing an approximately 0.1 N solution of it. The solution was standardized by iodometric titration with sodium thiosulfate [2].

To an aliquot part of the uranyl sulfate solution was added 1.5-2 fold excess of selenious acid solution, and enough alcohol to make its concentration ~ 50%. The pH of the solution was then adjusted to 4-5 by addition of a 5% aqueous solution of ammonium acetate. After leaving the precipitate to stand for one hour, it was filtered through a No. 42 Watmann filter paper, and washed several times with absolute alcohol to remove excess selenious acid. The uranium selenite was then dissolved in concentrated HCl and its selenium content determined iodometrically with sodium thiosulfate, using starch as indicator.

TABLE 1

Volume of UO_2SO_4 in ml	H_2SeO_4 added		$Na_2S_2O_3$ concentration, as N	Volume of $Na_2S_2O_3$ = H_2SeO_3 (reacted) in ml	Uranium found in g		Error in %
	ml	g			hydroxyquinoline method	selenite method	
10	10	0.04560	0.07180	12.10	0.05168	0.05170	0.04
15	15	0.06840	0.07180	18.10	0.07752	0.07734	0.22
10	10	0.05593	0.1285	12.75	0.09745	0.09752	0.07
20	20	0.09120	0.07180	24.20	0.1034	0.1034	0.00
20	20	0.1119	0.1285	25.50	0.1949	0.1950	0.05
40	45	0.2517	0.1285	50.50	0.3898	0.3862	0.81
{20	40	0.1824	0.07180	25.10	0.1034	0.1073	2.8}
{10	20	0.09120	0.07180	12.50	0.05168	0.05340	3.3}

Results of a number of tests showed that one mole of uranium is equivalent to one mole of selenite.

$$UO_2SO_4 + H_2SeO_3 \rightarrow UO_2(SeO_3) + H_2SO_4$$

from which it follows that 1 ml of 1 N $Na_2S_2O_3$ is equivalent to 0.05952 g uranium. Table 1 contains some typical experimental results.

It was established that the pH of the medium is an important factor in the quantitative precipitation of uranyl selenite; it should be kept between 4 and 5. This is readily achieved by addition of a small amount of a 5% solution of ammonium acetate. Since uranyl selenite hydrolyzes strongly in a pure aqueous solution, excess alcohol should be added beforehand to the solution of uranyl sulfate, till the alcohol concentration is at least 50%. Accurate and reproducible results were obtained when the amount of selenious acid added was not more than 1.5 - 2 times as much as the theoretical amount required for precipitation, according to the equation given above. A very large excess of selenious acid usually led to high results (see figures given in Table 1 in brackets). This can probably be attributed to the gelatinous character of uranyl selenite which adsorbs the H_2SeO_3, as a result of which complete removal of the acid is rather difficult. When the conditions given above are observed, the method is very suitable for determining uranium within a comparatively wide concentration range.

TABLE 2

Volume of UO_2SO_4 in ml	Uranium in g	$UO_2(SeO_3)$ in g		Difference
		Calculated	Found	
10	0.05168	0.08620	0.08630	0.0001
10	0.09745	0.1625	0.1622	0.0003
20	0,1034	0.1724	0.1726	0.0002
25	0.1292	0.2155	0,2174	0.0019
20	0.1949	0,3250	0,3244	0.0006

Since one mole of uranium combines with one mole of selenious acid, the formula of the selenite can be written in the form $UO_2(SeO_3) \cdot xH_2O$. In order to determine the water content this compound was filtered through a tared porous glass crucible, washed with absolute alcohol and acetone, and dried to constant weight. The results given in Table 2 show that the composition of the uranyl selenite corresponds to $UO_2(SeO_3)$.

The author wishes to thank Professor S. S. Djoshi for making it possible to carry out this work.

SUMMARY

Uranyl selenite is precipitated quantitatively on addition of an aqueous solution of selenious acid to a solution of a uranyl salt in 50% alcohol, at a pH between 4 and 5. The precipitate dissolves in concentrated HCl. A method is described for the volumetric determination of uranium, based on iodometric titration of liberated selenious acid. Results of the study indicate that the composition of the selenite can be represented by the formula $UO_2(SeO_3)$.

Received April 25, 1956

LITERATURE CITED

[1] J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry (Longmans, Green and Co., London, 1930), V. X, p. 820, 843.

[2] A. I. Vogel, A Text Book of Quantitative Inorganic Analysis (Longmans, Green and Co., London, 1948), p. 362.

BRIEF COMMUNICATIONS

METHODS OF BREAKING DOWN BARIUM SULFATE IN ORDER TO DETECT THE BARIUM ION IN IT QUALITATIVELY

G. I. Barannikov

Molotov Pharmaceutical Institute

During qualitative analysis for the identification of barium sulfate, the latter is boiled several times with concentrated sodium carbonate solution, or is fused with a mixture of sodium carbonate and potassium hydroxide, and the barium carbonate formed dissolved in nitric, hydrochloric, or acetic acids [1,2]. There is an indication [3], that barium sulfate dissolves to some extent in ammonium acetate. In pharmaceutical preparations, barium sulfate as impurity is determined after extraction with solvents [4]. The amount of $BaSO_4$ is determined from the weight remaining after extraction of the insoluble residue.

It is known that in the solid, white material, insoluble in acids, which remains during the normal method of qualtiative analysis, lead sulfate may be present in addition to barium sulfate. The latter can be detected and removed as follows. To a small amount of the dry test material contained in a beaker or test tube is added 1-2 ml of 30% hydrogen peroxide; after mixing, one drop of concentrated ammonia solution is added, and the whole shaken up; during this process lead sulfate is converted into a mixture of oxides. The process lasts no longer than a minute and is accompanied by evolution of a large amount of heat, and copious water vapor is given off.

When the reaction is complete, it can be readily seen visually, if lead were initially present, that there are yellow-brown particles of lead oxides as well as the colorless particles of barium sulfate present. The lead oxides, after removal of gaseous reaction products from the vessel by blowing, dissolve comparatively easily on boiling in excess dilute nitric acid. The precipitate is filtered off, and lead detected in the clear filtrate by means of the usual reagents: H_2S, H_2SO_4, CrO_4 ions, etc.

When there is no lead present, then after addition of hydrogen peroxide and ammonia, only colorless crystals of barium sulfate will be observed. In order to detect the barium ion which is not soluble in nitric acid, the residue is treated with orthophosphoric acid or heated as follows. A small amount of the barium sulfate powder is moistened with a few drops of concentrated phosphoric acid on the lid of a platinum crucible, and the mixture gradually heated in the top part of the flame of an alcohol burner (if heating is too rapid spluttering may occur). The reaction, which is accompanied by evolution of white fumes, lasts about 3-5 minutes and can be regarded as complete when the mass becomes completely colorless and transparent, while formation of bubbles of gas stops altogether. To the slightly warm material thus obtained is added 1-2 drops of concentrated nitric acid. When this is done, part of the solid material is converted into a friable colorless mass, which is readily soluble in some drops of water on heating [5]. This operation is repeated until all the barium sulfate has been brought into solution. The final solution obtained is then diluted with water, warmed until the solution is quite clear, and barium tested for. E.g., on addition to the solution obtained of some ammonia solution, followed by heating, a colorless precipitate of barium phosphate is formed, and after addition of concentrated sulfuric acid, formation of a fine crystalline precipitate of barium sulfate is observed. Barium sulfate can also be successfully broken down by using molten metaphosphoric acid or sodium hexametaphosphate [6].

The quickest way of breaking down barium sulfate is however by means of metallic magnesium as follows.

A piece of magnesium ribbon $\sim$5 cm long is covered on both sides at its middle with a thin layer of viscous vaseline, and the sticky surfaces touched to the finely ground barium sulfate powder. One of the ends of the ribbon is then held in a pair of tongs, and the other end ignited; the combustion products are transferred to a beaker, treated with excess hydrochloric acid, the solution brought to the boil, and finally filtered. Barium can then be detected in the clear filtrate obtained by means of the sulfate ion, and also by CrO_4^{-} ions in acetic acid.

SUMMARY

Methods are described for: 1) rapid separation of lead sulfate from barium sulfate by means of hydrogen peroxide in an ammoniacal medium; 2) dissolving barium sulfate in a mixture of nitric acid or hydrochloric acid and hydrogen peroxide; 3) breaking down barium sulfate by means of orthophosphoric acid and metallic magnesium, respectively.

Received November 5, 1951

LITERATURE CITED

[1] V. I. Petrashen, Qualitative Chemical Analysis (State Chem. Press, Moscow - Leningrad, 1948), pp. 176, 397.

[2] Treadwell and Hall, Qualitative Analysis (State Chem. Press, 1946), p. 298.

[3] V. F. Gillebrand and G. E. Lendel, Practical Textbook on Inorganic Analysis (United Sci. -Tech. Press, Moscow, 1935), p. 202.

[4] State Pharmacopeia of the USSR (Med. Press, 1946), VIII Edition, p. 79.

[5] Borneman, Inorganic Preparations (State Chem. Press, 1934), p. 68.

[6] B. V. Nekrasov, A Course of Inorganic Chemistry (State Chem. Press, Moscow - Leningrad), VIII Edition, p. 411.

PHOTO-NEPHELOMETRIC DETERMINATION OF MERCURIC CHLORIDE BY MEANS OF UROTROPINE AND POTASSIUM IODIDE

S. I. Kasyanenko

Pyatigorsk State Pharmaceutical Institute

Till recently there has been no photo-nephelometric method for determining mercury, apart from Gusev's method [1], in which antipyrine and potassium iodide in acid media were used as reagent. This method permits determination of 0.4 γ/ ml of Hg, with an accuracy of from ± 3 to ± 5%.

In our case we used a reaction proposed by Korenman [2], in which a mixture of potassium iodide and urotropine is used for detecting mercury. Hg^{2+} ions give a stable turbidity with a mixture of urotropine and potassium iodide, and this can be used for nephelometric determination of mercuric chloride in solutions. The limit of identification is 0.2 γ/ ml of Hg. Experimental error does not exceed ± 1.5%.

EXPERIMENTAL

Determinations were carried out as follows: to the test solution of $HgCl_2$ was added a known amount of 0.1 N solution of urotropine and potassium iodide, and the volume made up to 50 ml with distilled water. The turbid solution obtained was measured nephelometrically by means of a differential photonephelometer (galvanometer sensitivity $1.0 \cdot 10^{-8}$A). The concentration of urotropine and potassium iodide are important factors for getting a stable turbidity. In order to establish the optimum concentrations of urotropine and potassium iodide, constant known weights of mercuric chloride and potassium iodide respectively were taken, while the amount of urotropine was varied. The turbid solutions obtained were then measured nephelometrically.

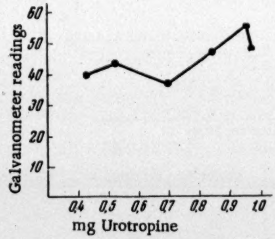


Fig. 1. Relation between amount of urotropine and galvanometer readings.

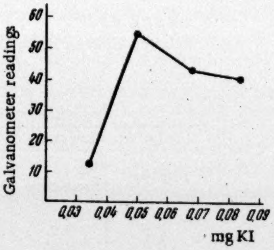


Fig. 2. Relation between concentration of potassium iodide in solution and galvanometer readings.

It is clear from Table 1 that at a urotropine concentration of 0.95 mg, the galvanometer gives a maximum reading. These relations are illustrated in Curve I (Fig. 1).

Similar results were carried out with varying $HgCl_2$ concentrations, viz. 0.3, 0.4, 0.5, 0.7, and 0.8 γ/ ml.

TABLE 1

Relation Between Amount of Urotropine and Galvanometer Readings

Taken for 1 ml reaction mixture of:			Galvanometer readings after:		
γ $HgCl_2$	mg KI	mg of Urotropine	2 minutes	4 minutes	6 minutes
0.6	0.05	0.4	40	39	39
0.6	0.05	0.56	43	43	42
0.6	0.05	0.70	38	37	37
0.6	0.05	0.84	46	45	45
0.6	0.05	0.95	55	55	55
0.6	0.05	0.98	48	47	47

TABLE 2

Relation Between Potassium Iodide Concentration in Solution and Galvanometer Readings

Taken for 1 ml of reaction mixtures of:			Galvanometer readings after:		
γ $HgCl_2$	mg of Urotropine	mgKI	2 minutes	4 minutes	6 minutes
0.6	0.95	0.034	11	11	11
0.6	0.95	0.05	55	55	55
0.6	0.95	0.068	43	43	43
0.6	0.95	0.086	41	41	41

TABLE 3

Relation Between $HgCl_2$ Concentration in Solution and Galvanometer Readings

1 ml of Solution contains			Galvanometer readings		
γ $HgCl_2$	mg of Urotropine	mgKI	2 minutes	4 minutes	6 minutes
0.5	0.7	0.065	50	50	50
0.6	0.95	0.065	55	55	55
0.7	1.16	0.068	60	60	60
0.8	1.23	0.085	65	65	65

TABLE 4

Determination of $HgCl_2$ by Ruppe's Method and Nephelometrically

$HgCl_2$ taken in g	$HgCl_2$ determined by Ruppe's method	Error in %	Determined nephelometrically	Error in %
0.5000	0.4874	—2.5	0.4922	—1.0
0.2500	0.2424	—3.0	0.2467	—1.3
0.1250	0.1212	—3.0	0.1233	—1.1

In the subsequent series of experiments, constant concentrations of $HgCl_2$ and urotropine, and varying concentrations of potassium iodide were used.

Results are given in Table 2.

It is clear from Table 2 that at a potassium iodide concentration of 0.05 mg, maximum galvanometer readings are obtained.

These relations are illustrated in Curve 2 (Fig. 2).

Similar experiments were carried out with various concentrations of $HgCl_2$, viz. 0.3, 0.4, 0.5, 0.7, and 0.8 γ/ml.

In order to construct a calibration curve, 0.5544 g of $HgCl_2$ was dissolved in a 100 ml standard flask. Standard solutions were then prepared from this solution with $HgCl_2$ contents varying from 0.5 to 0.8 γ/ml. Experimental results are given in Table 3 and Fig. 3.

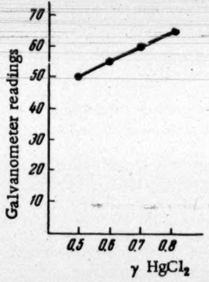


Fig. 3. Relation between $HgCl_2$ concentration in solution and galvanometer readings.

There is a linear relation between $HgCl_2$ concentration and galvanometer readings (Fig. 3).

The results given in Table 4 were obtained using our method, and that of Ruppe respectively [3-5].

The VII Edition of the USSR Pharmacopeia tolerates an error of 1.0%, while the VIII Edition tolerates 0.5%. Accordingly the method which we are putting forward is more accurate. The $HgCl_2$ to be determined nephelometrically should be dissolved in that volume of water which will ensure a concentration of $HgCl_2$ in it of 0.5 to 0.8 γ/ml.

1250 determinations were carried out during the course of this work.

In conclusion, I should like to thank Professor I. M. Dedyulin and V. N. Bernshtein for valuable advice.

SUMMARY

A method has been developed for the nephelometric determination of $HgCl_2$ by means of urotropine in the presence of potassium iodide. The method permits determination of 0.5 - 0.8 γ/ml of $HgCl_2$. The limit of identification is 0.2 γ/ml with an error of ± 1.5%.

Received March 5, 1954

LITERATURE CITED

[1] S. I. Gusev, J. Anal. Chem. 5, 6, 375 (1950).

[2] I. M. Korenman, Z. anal. Chem. 95, 4 (1934).

[3] Berl-Yunge, Chemico-Technological Methods of Research (State Chem. Press, 1941), Vol. III, No. II, p. 344.

[4] State Pharmacopeia of the USSR, (1942), VII Edition.

[5] State Pharmacopeia of the USSR (1946), VIII Edition.

THE OXALATE METHOD FOR DETECTING CADMIUM IN THE PRESENCE OF COPPER

M. P. Babkin

Donets Industrial Institute

Existing methods for detecting cadmium in the presence of copper are based on the following principles:

1) On differences in the oxidizing abilities of Cu^{2+} and Cd^{2+} ions respectively ($\epsilon_0 Cu^{2+}/Cu^0 = 0.314$; $\epsilon_0 Cd^{2+}/Cd^0 = -0.40$). Copper ions Cu^{2+} are reduced to metallic copper by iron [1], aluminum [2], sodium dithionate [3], chromous sulfate [4], or to insoluble cuprous compounds by means of potassium iodide [5], sodium thiosulfate [6,7], etc.

2) On complexing of copper ions into a stable complex by potassium cyanide [8], alkali tartrates [9,10], glycerol [11], ammonium thiocyanate [12], thiourea [13], etc. Cadmium ions can be detected as the sulfide directly in a solution containing complex copper ions [8, 12, 13], or after precipitation of cadmium hydroxide [9-11].

3) On precipitation of Cu^{2+} and Cd^{2+} as sulfides followed by dissolving of the cadmium sulfide in a hydrochloric acid solution of potassium iodide or ammonium chloride. Cadmium sulfide is precipitated from solution after addition of ammonia and ammonium sulfide [14].

4) On simultaneous complexing of copper ions as a soluble complex and precipitation of cadmium by one reagent – a mixture of ammonium chloride and sodium bicarbonate [15], potassium cyanate [16].

5) On separate precipitation of Cu^{2+} and Cd^{2+} ions respectively, at various pH values with quinaldinic acid [17, 18], and benzoquinaldinic acid [19].

6) On the volatility of metallic cadmium after separation of copper and cadmium as metals from the oxides by means of charcoal; the vapors of metallic cadmium combine with sulfur to form the sulfide [20].

Of these methods the most convenient and easy to carry out are those described in 2) and 4) above.

In the present article we demonstrate the possibility of detecting cadmium in the presence of copper by treating a solution containing these ions with excess of a saturated solution of ammonium oxalate. The precipitate of copper oxalate dissolves readily in excess ammonium oxalate to form the ion $[Cu(C_2O_4)_2]^{2-}$; the solubility of cadmium oxalate on the other hand, as can be seen from the following experiments, is negligible.

Into 25 ml of 0.1 N ammonium oxalate were introduced varying amounts of dry ammonium oxalate, and after dissolving it, and the solution being heated, 25 ml of a 0.1 N solution of cupric nitrate or cadmium nitrate was added. The precipitates of the oxalates of copper and cadmium were filtered after 2 days, washed, dissolved in sulfuric acid, and the oxalic acid given off titrated with potassium permanganate (Tables 1 and 2).*

When ammonium oxalate is present in 150% excess, copper oxalate is not precipitated; for an excess of ammonium oxalate up to 200% precipitation of cadmium oxalate improves, and only at a considerable excess of the oxalate ions (800%) does the amount precipitated drop (by 3.8%).

On the basis of these results, the following method is suggested for detecting cadmium in the presence of copper. To a solution containing both ions is added an excess of a saturated solution of ammonium oxalate, until the copper oxalate which is initially precipitated redissolves; the white precipitate of cadmium oxalate is separated, washed with water to free it from the blue complex of copper; the washed precipitate is then

---

* The results given in Table 1 were obtained by G. I. Novozhilov.

TABLE 1

Precipitation of copper oxalates in presence of excess of ammonium oxalate

Added $(NH_4)_2C_2O_4 \cdot H_2O$ (g)	Excess $C_2O_4^{2-}$ (%)	Precipitation CuC_2O_4 (%)
0.0	0.0	100.0
0.0444	25.0	86.6
0.0888	50.0	65.9
0.1332	75.0	43.8
0.1775	100.0	18.8
0.2663	150.0	—

TABLE 2

Precipitation of cadmium oxalate in presence of excess of ammonium oxalate

Added $(NH_4)_2C_2O_4 \cdot H_2O$ (g)	Bxcess $C_2O_4^{2-}$ (%)	Precipitation CdC_2O_4 (%)
0.0	0.0	100.0
0.355	200.0	100.3
0.71	400,0	99.8
1.065	600.0	98,0
1.42	800.0	96.2

treated with a solution of sodium sulfide; an orange yellow color of the precipitate indicates that cadmium is present. The crystalline precipitate of cadmium oxalate is freed readily from copper complex after 1-2 washes, which is an advantage when compared with separation of cadmium as the hydroxide from solutions of the glycerate or tartrate complex of copper [9-11].

During systematic analysis of a mixture of the cations of the sub-group IV, copper and cadmium dissolved as the ammines. In order to detect cadmium by the method suggested above, the ammine solution is evaporated to dryness in a porcelain basin on a water or air bath; the residue is moistened with a few drops of concentrated hydrochloric acid; the latter is removed by evaporation, and the residue dissolved in a small volume of water (0.5 - 1.0 ml); the solution is transferred to a centrifuge tube and if an insoluble turbidity remains in the solution it is removed; excess of a saturated ammonium oxalate solution is added dropwise with shaking until the blue color of the solution changes to a pale-blue; the white precipitate, insoluble in excess ammonium oxalate, is centrifuged off, washed with water, and treated with either a sodium sulfide solution or hydrogen sulfide water.

For low concentrations of Cd^{2+} it is recommended that the solution be left to stand for 10 minutes before separating cadmium oxalate from the solution containing the complex copper ions.

The limit of identification is 0.5 mg of cadmium in the presence of 20 times its amount of copper.

SUMMARY

A method is suggested for detecting cadmium ions in the presence of copper; it is based on complexing of copper ions as the complex ion $[Cu(C_2O_4)_2]^{2-}$ and precipitation of cadmium as a white precipitate of cadmium oxalate $CdC_2O \cdot 3H_2O$ with subsequent conversion of the latter into the sulfide.

Received April 2, 1955

LITERATURE CITED

[1] P. G. Popov, Ukrain. Chem. J. 3, No. 2 (1928).

[2] B. G. Tideman and B. V. Ozimov, J. Appl. Chem. 12, No. 3,468 (1939).

[3] P. G. Gaines and R. Woodriff, J. Chem. Educ. 26, 166 (1949).

[4] A. I. Busev and A. V. Zapolskaya, Trans. Commission Anal. Chem. 3, (6), 337 (1951).

[5] N. S. Krutovoi, Trans. Commission Anal. Chem. 3 (6), 225 (1951).

[6] Vortman, Z. anal. Chem. 20, 416 (1881).

[7] J. Sarudi, Z. anal. Chem. 127, 161 (1944).

[8] V. P. Treadwell and V. T. Hall, Qualitative Analysis (State Chem. Press, Moscow - Leningrad, 1946). p. 553.

[9] I, R. McReynolds, J. Chem. Educ. 17, 532 (1940).

[10] Grillot and Kelley, Ind. Eng. Chem., Anal. Ed. 17, No. 7 (1945).

[11] A. I. Busev, Bull. Mendeleev All-Union Chem. Soc. 1940, No. 10,13.

[12] V. N. Podchainova, Factory Lab. 18, No. 4,400 (1952).

[13] A. Pilipenko and G. S. Lisetskaya, Ukrain. Chem. J. 19, 88 (1953).

[14] I. M. Korenman, Sci. Records Gorky State Univ. 1949, No. 15.

[15] G. M. Karns, J. Am. Chem. Soc. 48, 2626 (1926).

[16] M. V. Davis and F. H. Heath, J. Chem. Educ. 26, 277 (1949).

[17] A. K. Majumdar, Analyst 68, 242 (1943).

[18] C. E. Pritchard and R. C. Chirnside, Analyst 68, 244 (1943).

[19] A. K. Majumdar and A. K. De, J. Indian Chem. Soc. 29, 499 (1952); Chem. Abs. 47, No. 6, 2628 (1953).

[20] F. A. van Atta and W. L. Wasley, J. Chem. Educ. 18, No. 1 (1941).

BLANK
PAGE

DETECTION OF CADMIUM IN THE PRESENCE OF COPPER

A. D. Despiller, M. A. Gurinovich, and Yu. N. Anisimova

Vinitsky Medical Institute

The following method of detecting cadmium in the presence of copper is described in a widely used textbook on analytical chemistry: "If Cu^{2+} has been found, then 2N H_2SO_4 is added to the solution in such amount that the blue color of the complex $[Cu(NH_3)_4]^{2+}$ changes to the blue color of the Cu^{2+} ion. When this point has been reached some more H_2SO_4, equal in volume to one third of the total solution, is added. The acid solution obtained is heated with a lump of metallic zinc until the blue color of the copper ion Cu^{2+} disappears completely. Under these conditions, Cu^{2+} is reduced by zinc to the metal. The latter is filtered off and put aside". Cadmium is then detected in the filtrate by means of hydrogen sulfide. This method of separating copper and cadmium is based, apparently, on the assumption that zinc, which can precipitate copper in acid media, cannot precipitate cadmium [1,2].

Sergeev [3], however has noted that zinc does displace cadmium from acid solutions of its salts. Our experiments also showed that metallic zinc filings tied up with a thread in a tight bundle in fine cigarette paper, displace cadmium both from a concentrated solution of the chloride and acetate in concentrated hydrochloric acid, and from a 0.2 N solution of chloride in hydrochloric and sulfuric acid (1:2), and, also from a number of dilute acidified solutions of cadmium salts. Precipitation is detected on the surface of the bundle. The accompanying diagram shows a microphotograph of dendrites of metallic cadmium, obtained from a concentrated solution of cadmium sulfate in sulfuric acid (1:1). The solution was strongly acid after precipitation of cadmium.

Cadmium is completely displaced by zinc even from a strongly acid solution, e.g. from a mixture of equal volumes of a 1N solution of its sulfate and 7 N H_2SO_4 on heating for 3-4 hours. Cadmium can be rapidly displaced from 1 N $CdSO_4$ in concentrated HCl in the cold. Special experiments showed that cadmium can be detected in metallic copper long before complete removal of the latter by zinc, when the solution of the mixture of copper and zinc salts is still bright blue. Thus, both metals are precipitated simultaneously. All the facts adduced lead one to conclude that the method recommended for detecting cadmium in solutions containing copper [1], is incapable of giving satisfactory results. This conclusion received confirmation. In Table 1 are given results of several typical experiments.

In order that our conditions should approximate to those used in systematic analysis, we added an equal volume of 2 N $(NH_4)_2SO_4$ to a mixture of solutions of cupric sulfate and cadmium sulfate, followed by 1/3 of the total volume of 2 N H_2SO_4.

TABLE 1

Volume of $CuSO_4$ solution in ml	$CuSO_4$ concentration in N	Volume of $CdSO_4$ in ml	$CdSO_4$ concentration in ml	Atomic ratio Cd/Cu	Results of Cd detection
0.5	1.0	0.5	1	1	Not detected
0.2	0.2	0.5	0.2	2.5	»
0.5	0.2	0.5	1	5	Detected
0.25	0.2	0.5	1	10	»

0.0104 g of $CdSO_4$ in 0.7 ml of solution could not be detected in the presence of 1/2.5 its amount of copper.

The results obtained demonstrate how insensitive the proposed method for detecting cadmium is, and how necessary it is to find an improved method.

I. Replacement of Zinc by Aluminum During Separation of Cadmium from Copper

A number of experiments which we carried out showed that aluminum, in contrast to zinc, displaces cadmium only with great difficulty. This fact may be illustrated by the following test. Into two test tubes are poured a 1 N solution of cadmium sulfate acidified with sulfuric acid. In one of the test tubes is immersed a packet made of fine cigarette paper containing zinc fillings, while in the other a similar packet containing aluminum filing is immersed. In the first instance, a positive reaction is obtained quickly and distinctly, while in the second case either a negative result is obtained, or it is only extremely weakly positive.

These facts allow one to suggest that on substituting aluminum for zinc, it should be possible to precipitate copper from its salts without precipitating appreciable amounts of cadmium which might be present in the solution at the same time. In such cases, after precipitation of copper, cadmium can be detected in the filtrate with a solution of sodium sulfide; the sensitivity of the reaction is high. Results are given in Table 2 of experimental of experiments carried out on detection of cadmium with sodium sulfide after precipitation of copper with zinc and with aluminum respectively, in parallel tests.* Positive or negative results respectively are indicated by + or -. Precipitation was carried out with heating. The solution, after addition of metal, was heated for 2 minutes on a water bath and left; it was removed from the water bath 2 minutes before adding sodium sulfide. In all cases heating should be continued till the color of the copper ion has disappeared completely.

TABLE 2

Concentration		Volume of solution in ml		Total amount in mg		Atomic ratio Cu/Cd	Acid concentration	Displacement by	
$CuSO_4$	$CdSO_4$	$CuSO_4$	$CdSO_4$	Cu	Cd			Aluminum	Zinc
0.1524	0.1428	0.05	0.05	0.24	0.40	1.07	2 N H_2SO_4	+	—
0.1524	0.1428	0.02	0.02	0.097	0.16	1.07	Neutral	+	—
0.0762	0.0714	0.05	0.05	0.12	0.2	1.07	»	+	—
0.0762	0.0714	0.02	0.02	0.048	0.08	1.07	»	+	—
Higher atomic ratios									
0.686	0.0714	0.25	0.25	5.4	1.0	9.6	2 N H_2SO_4	+	—
0.686	0.0714	0.5	0.5	10.8	2.0	9.6	2 N H_2SO_4	+	—
0.686	0.0714	0.05	0.05	1.08	0.2	9.6	Neutral	+	—
0.686	0.0714	0.025	0.025	0.54	0.10	9.6	»	+	—

---

* During work with small volumes of liquid, precipitates are removed from solution by centrifuging.

It is clear from these results that substitution of aluminum for zinc, during separation of mixtures of copper and cadmium, leads to an appreciable increase in the sensitivity of cadmium detection. Detection of cadmium in mixtures of the chlorides of cadmium and copper, after precipitation of copper by aluminum, gives less satisfactory results: the sensitivity of the method in this case is also somewhat lower.

II. Analysis of Mixtures of Cadmium and Copper Nitrates

Tests showed that both zinc and aluminum hardly precipitate cadmium at all from not too acid solutions of their nitrates. At the same time these metals readily displace copper from its nitrate, both in neutral and in acid media.

An unacidified solution of a mixture of copper and cadmium nitrates, after precipitation of copper, can be kept for several hours in contact with aluminum metal or zinc metal, without deposition of cadmium.

TABLE 3

Concentration		Volume in ml		Acidity	Content in mg		Atomic ratio Cu/Cd	Displacement by	
$Cu(NO_3)_2$	$Cd(NO_3)_2$	$CuSO_4$	$CdSO_4$		Cu	Cd		Aluminum	Zinc
0.686	0.0714	0.05	0,05	Neutral	1.09	0.2	9.6	+	+
0.686	0.0714	0.025	0,025	»	0.54	0.1	9.6	+	—
0.00762	0.00714	0.05	0,05	$2\,N$ H_2SO_4 + + $(NH_4)_2SO_4$	0.012	0.02	1.06	+	+
0.00762	0.00714	0.025	0,025	$2\,N$ H_2SO_4 + + $(NH_4)_2SO_4$	0.006	0.01	1.06	Very weak	—

Results of tests for establishing what are the minimum amounts of cadmium which can be detected after removal of copper from nitrate solutions, are given in Table 3. (Tests were carried out with heating till complete disappearance of the characteristic color of copper ions).

Experiments carried out in the presence of ammonium nitrate gave similar results. Accordingly, the sensitivity of detection of cadmium by sodium sulfide, after removal of copper by aluminum, in neutral or weakly acid solutions of the nitrates, is high enough. The reaction can be used in the course of systematic analysis, after the mixture of the ammines of cadmium and copper has been neutralized with nitric acid.

Equally valuable results can be obtained by displacing copper with iron on heating in the presence of excess 6 N HCl as is recommended in Treadwell and Hall. In this case however, cadmium, naturally, cannot be detected by means of sodium sulfide.

SUMMARY

A method has been developed for the separation of copper from cadmium by means of metallic aluminum, which is suitable for systematic qualitative analysis.

Received May 8, 1951

LITERATURE CITED

[1] V. N. Alekseev, A Course of Analytical Chemistry (State Chem. Press, 1949), p. 151.

[2] F. P. Treadwell and V. T. Hall, Qualitiative Analysis (State Chem. Press, 1946), p. 61.

[3] A. P. Sergeev, "Reactions for Metals of the Hydrogen Sulfide Group", Pharmaceutical J.,1929.

BLANK
PAGE

DETECTION OF BERYLLIUM IONS

V. K. Zolotukhin

The I. Franko Lvov State University

Beryllium hydroxide reacts with the fluorides of the alkali metals to form alkali according to the equation:

$$Be(OH)_2 + 4F \rightleftharpoons [BeF_4]^{2-} + 2OH^-.$$

The alkali formed during the reaction can be detected by means of a suitable indicator, e.g. phenolphthalein. We have shown previously the possibility of carrying out a quantitative determination of beryllium on the basis of the reaction indicated [1]. The present note is concerned with the use of this reaction between beryllium hydroxide and potassium fluoride for detecting Be^{2+}.

Detection of beryllium in its salts, on the basis of the reaction with fluorides just indicated was carried out as follows. To 1-2 drops of test solution of beryllium salt is added some alkali to the bright red color of phenolphthalein; 0.01 acid is then added till the solution becomes colorless (the solution is also decolorized by the action of atmospheric CO_2 on shaking it in a test tube). Next a few drops of a ~ 1 N KF solution neutralized to phenolphthalein is added. The appearance of a rose color when this is done testifies to the presence of Be^{2+}. Having added 0.1 - 0.01 N acid dropwise till the solution is decolorized, it is possible to get an approximate idea of the amount of Be^{2+} that can be detected qualitiatively.

For detection of beryllium ions, the limiting dilution proved to be approximately 1:2, 500,000, while the limit of identification is 0.4 γ (in 1 ml of solution).

Detection of Be^{2+} by the fluoride method in the presence of Al^{3+} is impossible in view of the fact that aluminum hydroxide also reacts with fluoride ions to form OH'. Hydroxides of of the other cations of the third analytical group do not react with alkali metal fluorides to give appreciable amounts of alkali; all the same, the presence of appreciable amounts of these cations complicates, or makes it impossible, to carry out exact neutralization of the test solution, and consequently, detection of Be^{2+} in it.

Be^{2+} can be separated from Al^{3+} by various means [2]. We used sodium bicarbonate for this purpose.

Test solutions containing Be^{2+} and Al^{3+} were treated with a 1-2 fold excess of $NaHCO_3$ (as 1 N solution) and boiled for 1-2 minutes. The solution plus precipitate is then cooled, neutralized with 0.1 N hydrochloric acid till the phenolphthalein is colorless (in order to decompose aluminates) and filtered. The filtrate is acidified with 2N hydrochloric acid, heated to the boil (to remove CO_2), cooled, and neutralized with 1-0.01 N sodium hydroxide to a phenolphthalein end point.

The minimum amount of Be^{2+} which can be detected by the fluoride method, in the presence of 150 times its amount of Al^{3+}, separated by sodium bicarbonate, is ~ 3γ (in 1 ml solution).

Separation of Be^{2+} from other cations of the third group (apart from Al^{3+}) is carried out with ammonia, and then with sodium hydroxide, and hydrogen peroxide [2].

Since $NaHCO_3$ precipitates cations of the third analytical group on heating, we detected beryllium by the fluoride method, after its removal from all other cations of the third group with sodium bicarbonate. The method of separating Be^{2+} from other cations of the third group, and its subsequent determination was the same as that used for separating Be^{2+} from Al^{3+}.

It was shown experimentally that the minimum amount of Be^{2+} which can be detected by the fluoride method in the presence of 25 times its amount of Cr^{3+}, Al^{3+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, (in equivalent amounts), after separation with NaHCO$_3$ is equal to $\sim 8\ \gamma$ (in 1 ml solution).

SUMMARY

A method is described for detection of beryllium which is based on interaction of Be(OH)$_2$ with alkali metal fluorides to form OH ions which leads to reddening of phenolphthalein. The limiting dilution is 1: 2, 500, 000, while the limit of identification is 0.4 γ Be in 1 ml. Beryllium must be separated beforehand from other ions.

Received November 22, 1954

LITERATURE CITED

[1] V. K. Zolotukhin, J. Anal. Chem. 6, 246 (1951).

[2] N. I. Blok, Qualitative Chemical Analysis (State Chem. Press, 1952), p. 308, 352.

DISCUSSION

DIFFUSION OF ELECTROLYTES AND THE POLAROGRAPHIC METHOD

REPLY TO Ya. P. GOKHSHTEIN

K. Micka and A. Vlcek

Polarographic Institute of the Czechoslovakian Academy of Sciences, Prague

There are, in our opinion, some inaccuracies and errors in Ya. P. Gokhshtein's reply "Apropos Observations Made by K. Micka and A. Vlcek" [1], and in the article "Diffusion of Electrolytes and the Polarographic Method"; we should like therefore to go into some of the points under discussion in more detail, and to give, if possible, some decisive answers to some debatable questions which will not admit of more than one interpretation.

The major points under discussion are the following (see e.g. [2]):

1) Gokhshtein states [3], that the limiting polarographic current of a given ion, in the presence of an indifferent electrolyte, consists of the diffusion current and an "additional current".

2) Gokhshtein states [3], that the "additional current", which does not obey Ilkovich's equation, amounts to, on a average, ± 0.23% of the diffusion current. For the limiting current, he gives the equation $I_1 = I_d \pm 0.23 I_d$.

3) Gokhshtein [3], on the basis of his experiments and on theoretical grounds, states that Heyrovsky and Ilkovich's theory on the effect of the concentration of the indifferent electrolyte on the limiting current of the deplorizing ion, is incorrect, and that the transport number of the ion does not tend to zero with increasing concentration of supporting electrolyte.

Let us first of all turn our attention to the "additional current". If this current were determined by some factors which have nothing in common with the nature of the depolarizing ion (corrections for spherical diffusion, convection caused by the outflow and dropping of the mercury, improverishment of electrolyte in depolarizing ions are of this type), one should expect that it would be at least approximately the same for all ions. On the contrary, according to Gokhshtein [3], deviations from Ilkovich's equation vary from -26.2% to 30.5% for various depolarizers. Convection, caused by the outflow of mercury at discharge rates of up to 2 mg/sec, and supporting electrolyte concentrations (e.g. sodium chloride) of up to 3M is immeasureably small [4]. The weak movement of electrolyte caused by break-off of the drop, has no effect on i – t curves [5]. Corrections for spherical diffusion [6], always lead (for depolarizers in solution) to a small increase in the calculated value of the current (for a more detailed discussion, see [7]). The effect of a drop in concentration (improverishment) of the depolarizing agent in the neighborhood of the electrode has been studied by Vlcek [7], Hans et al. [8], and Smoler [9]. This improverishment is clearly marked on i – t curves, chiefly during the initial stages of drop growth. It follows from Smoler's experiments that depletion of electrolyte near the electrode has the effect of lowering the average current by 5-7% as compared with the current in a non-depleted solution. This is partly compensated by the effect of spherical diffusion.

Further, it is possible that the "additional current" is caused by factors which are characteristic of a given depolarizer; from these we however, have earlier excluded the effect of ionic migration, in view of the fact that there is excess indifferent electrolyte in solution. There remains thus, the effect of changes in diffusion coefficient; nothing is known about such changes yet. Gokhshtein himself regards this diffusion coefficient as constant in a given solution.

In his last article, Gokhshtein [1], incorrectly relies on the results of Hans and coworkers [8], according to whom the equation $i_d = 708nD^{1/2} m^{2/3} t^{1/6}(1 + Ay + By^2)$ with a numerical factor of 708, approximating to Gokhshtein's factor of 744.2, hold good. This equation however is only correct for a momentary current, and, consequently, comparison with Gokhshtein's equation for the average current has no meaning at all. With the exception of small correction factors (Ay, By^2), the equation adduced by Hans and coworkers is in complete agreement with Ilkovich's equation for a momentary current.

Hans' statement [8], to which Gokhshtein refers [1], that turbulent movement is manifested at discharge rates exceeding 1 mg/sec, is based on a comparison of i— t curves in the presence and absence of gelatin respectively. The difference observed is very small, and the influence of gelatin cannot be regarded as constant; accordingly reliable conclusions cannot be drawn on the basis of such observations. According to Micka [4], no turbulent movement is observed in solutions of usual purity, at discharge rates up to 2 mg/sec, in accordance with Vlcek's results [7].

As for diffusion coefficients, one just cannot finally decide yet which values are correct, and which are not. Gokhshtein states that the diffraction micro-method gives reliable results. In this connection it is necessary to point out that methods based on measurements of light refraction may lead to incorrect results, if the rate at which ions of the indifferent electrolyte move is mutually comparable to that of the test ions. [10.11]; in other words if there is not a sufficient excess of indifferent electrolyte. This condition was observed only in some of Gokhshtein's experiments [12]; in others the ratio of the concentrations of test ion to indifferent electrolyte varied from 1:20 to 1:1 (e.g. Pb^{2+} in 0.12 M KNO_3 [12], some values for Cd^{2+} in 1 M KCl and for IO_3' in 0.1 M KNO_3 [13]). In his paper [3], Gokhshtein states that at concentrations where the excess of potassium chloride is more than 20 times that of the cadmium chloride, the diffusion coefficient is practically independent of potassium concentration; later on [3], he states that the diffusion coefficient of iodate ions in solutions of 0.1 M KNO_3, 0.02 M KOH, and 1 M KOH, is the same and is equal to $16.3 \cdot 10^{-6}$ cm^2/sec. Despite this result, he tries to show that an indifferent electrolyte has an appreciable effect on the diffusion coefficient of the given ion.

The correctness of the Ilkovich equation for the mean diffusion current has been verified recently [13], by extrapolation of the diffusion coefficient calculated from the Ilkovich equation to zero ionic strength. The extrapolated diffusion coefficient satisfies the theoretical value obtained by means of Nernst's formula with an accuracy of up to 7%.

Gokhshtein in his work [3,12], used the incorrect formula for the transport number of the ions, and on this basis he shows that the Heyrovsky-Ilkovich equation is not applicable to the migration current , and the transport number of the ion in the presence of excess electrolyte is not equal to zero. We have already pointed out this fact to Gokhshtein [2]· nevertheless we think that it is necessary to emphasize this point again, because Gokhshtein still uses this incorrect equation.

The Heyrovsky-Ilkovich equation for the migration current ($i_m = ni_d$) cannot represent experimental results accurately, even after correcting for changes in diffusion coefficient, since these are not derived on the basic differential equations for diffusion of an electrolyte in an electric field. In essence, however, this equation is correct, as Gokhshtein himself acknowledges [1].

Finally we should again like to express our opinion that the "additional current" theory of Gokhshtein has no substantial basis, and that, in fact, what we have to deal with are experimental errors. On the basis of our own work and on that of others we can affirm that the "additional current" of Gokhshtein has no real existence, and that the Ilkovich equation, under conditions which exclude turbulent flow and migration, can be applied with reasonable accuracy [7].

Received April, 1956

LITERATURE CITED

[1] Ya. P. Gokhshtein, J. Anal. Chem. 10, 192 (1955) (T.p. 181)*

---

* T.p. = C. B. Translation pagination.

[2] K. Micka and A. A. Vlcek, Chem. Listy 48, 923 (1954); Collection of Czechoslov. Chem. Commun. 19, 842 (1954).

[3] Ya. P. Gokhshtein, J. Anal. Chem. 8, 71 (1953) (T.p. 77).*

[4] K. Micka, Chem. Listy 49, 1148 (1955).

[5] K. Micka and I. Smoler, Chem. Listy (in press).

[6] J. Koutecky, Czechoslov. J. Phys. 2, 117 (1952); Czechoslov. J. Phys. 2, 51 (1953).

[7] A. A. Vlcek, Chem. Listy 47, 1440 (1953).

[8] W. Hans, W. Henne and E. Meurer, Z. Elektrochem. 58, 836 (1954).

[9] I. Smoler (not published).

[10] R. B. Dean, J. Am. Chem. Soc. 67, 31 (1945).

[11] J. R. Vinograd and J. W. McBain, J. Am. Chem. Soc. 63, 2008 (1941).

[12] Ya. P. Gokhshtein, J. Phys. Chem. 26, 224 (1952).

[13] K. Micka, Chem. Listy 50, 203 (1956).

---

* T.p. = C. B. Translation pagination.

BLANK
PAGE

DIFFUSION OF ELECTROLYTES AND THE POLAROGRAPHIC METHOD

A REPLY TO THE PRECEDING ARTICLE BY K. MICKA AND A. VLCEK

Ya. P. Gokhshtein

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow

The present article is in reply to the second communication by Micka and Vlcek and is a continuation of the discussion [1]. In their second communication Micka and Vlcek, in addition to some new questions, have touched again on some questions that have already been dealt with in my first reply [2]; this relates in particular to Micka and Vlcek's statement on the contradication between results [3], and those of other authors.

The incorrectness of this statement of theirs has already been demonstrated in the first reply, where tables of results obtained by Vinograd, McBain, Kabanov, Rulfs, et al.were given. The effect of the indifferent electrolyte and mixing was considered in no less detail; we will not dwell on these points again, but rather try to clear up a number of newly posed questions, in the interpretation of which, Micka and Vlcek made a number of mistakes; to this number belong questions relating to the additional current, the multiplier in Hans' equation for the mean current, and transport numbers.

In their new communication with which they have opened the discussion, there are several categorical denials.

They make a special point of attacking the impossibility of comparing the equation given by Hans et al. [4]

$$I_{\max} = 708nD^{1/2}cm^{2/3}t^{1/6}\,[1 + 39D^{1/2}m^{-1/3}t^{1/6} + 3000Dm^{-2/3}t^{1/3}] \qquad (1)$$

with the equation

$$\bar{I}_{\text{lim}} = 744ncD^{1/2}m^{2/3}t^{1/6}. \qquad (2)$$

"Hans' equation is only valid for a momentary current, and, consequently," in their own words, "comparision has no sense"; then further, "with the exception of small correction factors (Ay, By^2), the equation adduced by Hans et al. is in complete agreement with Ilkovich's equation for momentary current". These statements call for two objections:

In the first instance, to deny the sense in comparing the two equations is not convincing, because derivation of Hans' equation for the mean current from his equation for momentary current has just as much sense as the generally accepted transformation of the maximum current of Ilkovich to a mean current. The idea of comparing equations for mean currents with Expression (2) is obvious.

Secondly, Micka and Vlcek's mistake is to underestimate the factors Ay and By^2. The authors, apparently, are prejudiced that these factors are small in value. Nevertheless, calculation indicates that their sum is of the order of 0.10 - 0.20 (10-20%) of the current and more (for more details see below).

Finally, there is the close agreement between the multpliers in Equations (1) and (2). To avoid dwelling on one point of the discussion, where Micka and Vlcek have understood comparing the multipliers to mean comparison of the numbers 708 and 744, we should like to point out that the "multiplier" must be a constant optionally. The multiplier in Hans' equation will not be 708 or 607, but

$$708(1 + Ay + By^2) \text{ momentary current}$$
$$607(1 + A'y + B'y^2) \text{ average current}.$$

Let us make a quanitative estimation of the multiplier. Taking the mean over the interval (0, t) leads us to Hans' equation for the average current:

$$\overline{I}\text{lim} = \frac{1}{t}\int_0^t (708nD^{1/2}cm^{2/3}t^{1/6} + 708\cdot 39ncm^{1/3}t^{1/3}D + 3000\cdot 708nct^{1/2}D^{3/2})\,dt$$

or, after integration: $1{,}415\cdot 10^6nct^{1/2}D^{3/2} + 2{,}071\cdot 10^4ncm^{1/3}t^{1/3}D + 607ncm^{2/3}t^{1/6}D^{1/2} - I_{\text{lim}} = 0.$ (3)

This is an equation of the third degree with respect to $D^{1/2}$. For m and t varying in the limits (0.7 - 4.5 mg/ sec), (2 - 8 sec), it gives, as well as two imaginary roots, one real root

$$[\alpha^3 + \beta^2 > 0;\ \alpha = 1{,}191\cdot 10^{-4}m^{2/3}t^{-1/3};\ \beta = 9{,}3\cdot 10^{-7}mt^{-1/2} +$$
$$+ 3{,}534\cdot 10^{-7}(nc)^{-1}t^{-1/2}\overline{I}\text{lim}].$$

The latter can be determined without difficulty by means of the formula

$$D = \left(\sqrt[3]{\beta + \sqrt{\beta^2 + \alpha^3}} + \sqrt[3]{\beta - \sqrt{\beta^2 + \alpha^3}} - \frac{a}{3}\right)^2, \qquad (4)$$

where $a = 1.464\cdot 10^{-2}\,m^{1/3}t^{-1/6}$.

TABLE 1
Diffusion Coefficients of Tl^+ and Pb^{2+} in 0.1 N KCl
(Strehlow and Stackelberg's results were used for calculation [5]).
0.002 N TlCl in 0.1 N KCl + 0.01% gelatin

Capillary	Height of mercury column in cm	m in mg/ second	Dropping time t in seconds	I_{limiting} in μA	Diffusion current constant according to Ilkovich	$D_{Tl}10^6$ cm²/sec. by Ilkovich's equation	$D_{Tl}10^6$ cm²/sec. by Han's equation	Deviation between the values for D, in %
I	47	2.791	4.40	14.13	2.780	21.10	15.80	25.1
II	30	0.966	5.78	7.398	2.806	21.65	14.15	34.6
	50	1.640	3.40	9.560	2.794	21.50	15.40	28.4
IV	25	0.805	6.32	6,638	2.822	21,70	13.90	36.0

0,001995 M Pb^{2+} in 0,1 N KCl + 0,01% gelatin

						$D_{Pb^{2+}}\cdot 10^6$. cm²/sec.		
I	30	1.408	5.67	13.38	3.996	10.92	8.28	24.2
	40	1.902	4.30	15.33	3.925	10.47	8.28	20.9
	20	0.9026	8.86	10.66	3.976	10.77	7.66	28.9

It is possible, by substituting known diffusion coefficients in Hans' equation, to determine the value of the multiplier 607 $(1 + A'y + B'y^2)$.

Let us first calculate diffusion coefficients (D) on the basis of Hans' equation and compare them with D found from Ilkovich's equation. In order to forestall any doubts that Micka and Vlcek may have on the absence of experimental error, we shall use Strehlow and Stackelberg's results [5], (I_{limiting}, m and t). The results given in Table 1 show that the diffusion coefficients of Tl^+ and Pb^{2+} differ by 21-36% from D calculated on the basis of Ilkovich's equation, while the values of D_{Tl} are in good agreement with D according to Rulfs [6], and the diffraction micro-method [7,8]. If one substitues D found on the basis of Hans' equation in the Ilkovich equation, the limiting currents for thallium and lead will be 11-20% less than the experimental values. Thus, deviations from Ilkovich's equation are established by Hans' equation.

TABLE 2

Value of the Multiplier in the Equation of Hans' et al.

0.002 N TlCl in 0.1 N KCl, containing 0.01% gelatin; D_{Tl} according to Rulfs [6] = $16.7 \cdot 10^{-6}$ cm^2/ second

m in mg/ second	Dropping time t in seconds	I_{limiting} found by [5], in μA	Value of the multiplier in Hans' equation [4], K
2.791	4.40	14.13	689.66
2.326	2.42	11.24	685.92
1.640	3.40	9.56	704.20
1.271	4.20	8.344	722.59
0.966	5.78	7.398	742.48
0.805	6.32	6.638	756.36

From Table 2 it is clear that the multiplier 744 lies within the range for K, 689-756. If we use diffusion coefficients calculated on the basis of Ilkovich's equation (see Table 1), for our original results, the values of K will be even higher, and the multiplier 744 will be nearer to the lower limit. Thus, the statement on relatively close agreement between the coefficient 744 and the multiplier K is confirmed by calculation. Micka and Vlcek's opinion on the agreement between the Ilkovich and Hans equations respectively is not justified.

As for Hans' own opinion, he also comes to the conclusion that "Ilkovich's equation is not applicable to exact calculation of limiting polarographic currents" [4].

Let us now turn to the expression for the deviations. The latter require exact quantitative evaluation, and here, it should be pointed out that the expression

$$I_{\text{limiting}} = I_{\text{diffusion}} + 0.23 I_{\text{diffusion}} \qquad (2)$$

is inferior in many respects to Hans' formula, though it is near to the results of the latter. Formula (2) appeared before Hans' equation was suggested, and was based on experimental results from which it was derived by averaging. Consequently, it cannot follow all the changes in m and t – which are the disadvantages of this formula. If one understands the deffects of (2) only in this sense, then it is possible to agree with the opinion of Micka and Vlcek on this question.

Let us now turn to the question of transport numbers. When determining transport numbers in an electrolyte consisting of two types of cations, two cases can arise: 1) reduction of only one of the cations; 2) both types of cations participate in the electrochemical reaction.

It is obvious that if the formula

$$T_i = \frac{c_i \lambda_i}{\sum\limits_{k=1}^{3} c_k \lambda_k} \qquad (5)$$

holds for the second case, then it will require modification for the first.

Let us consider the case of Expression (3), In the solution there are Cd^{2+}, K^+, and Cl' ions. KCl is the indifferent electrolyte here and consequently it is the limiting current of Cd^{2+} and the reduction potential corresponding to it which is of primary inportance to us. At this potential K^+ will still be unreduced. Micka and Vlcek suggest that in this case the following formula should be used:

$$T_{Cd^{2+}} = \frac{c_{Cd^{2+}}\lambda_{Cd^{2+}}}{c_{Cd^{2+}}\lambda_{Cd^{2+}} + c_{K^+}\lambda_{K^+} + c_{Cl^-}\lambda_{Cl^-}}. \qquad (6)$$

But then, by what expression for t will the simultaneous reduction of Cd^{2+} and K^+ be described? It would seem that Formula (6) would fit.

Differences between the two cases are obvious. If, even during the first moments of hydrolysis, the K^+ components in the current will be the same in both cases, then in the course of time, they will change differently. In the first case, the K^+ component will rapidly drop to zero, while, in the second case, it will remain constant. This difference does not allow one to use one formula for both cases.

If K^+ is not reduced, then, after its distribution in solution, it does not participate in transporting the current, and its influence is restricted to weakening the electric field of the cathode.

Other authors who have occupied themselves with this question, have put forward equations for the migration current, which differ essentially from that used by Micka and Vlcek (see, e.g. the work of Levich [9], and Kolthoff and Lingane [10]).

Received May 7, 1956

LITERATURE CITED

[1] K. Micka and A. A. Vlcek, Chem. Listy 48, 923 (1954); Collection of Czecheslov. Chem. Commun. 19, 841 (1954).

[2] Ya. P. Gokhshtein, J. Anal. Chem. 10, 192 (1955) (T.p. 181).*

[3] Ya. P. Gokhshtein, J. Anal. Chem. 8, 71 (1953) (T.p. 77).*

[4] W. Hans, W. Nenne and E. Meurer, Z. Elektrochem. 58, 836 (1954).

[5] H. Strehlow and M. V. Stackelberg, Z. Elektrochem. 54, 51 (1950).

[6] Z. Charles Rulfs, J. Am. Chem. Soc. 76, 2071 (1954).

[7] Ya. P. Gokhshtein, J. Phys. Chem. 26, 224 (1952).

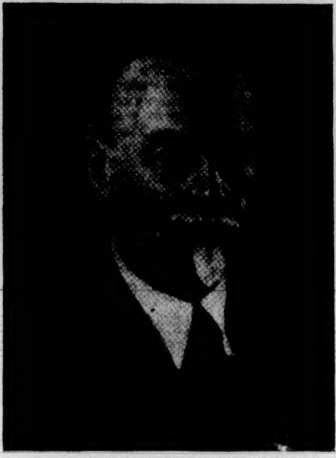
[8] Ya. P. Gokhshtein, J. Phys. Chem. 28, 1417 (1954).

[9] V. G. Levich, Physico-Chemical Hydrodynamics (Acad. Sci. USSR Press, 1952), pp. 419-424.

[10] I. M. Kolthoff and J. J. Lingane, Polarography (1952), p. 126-127

---

* T.p. = C. B. Translation pagination.



ALEKSEI MIKHAILOVICH VASILEV

(1882 - 1956)

Professor Aleksei Mikhailovich Vasilev, one of the oldest analytical chemists of our country, who held the chair of analytical chemistry in Kazan University and Kazan Chemico-Technological Institute, and was a Doctor of Chemical Sciences died on April 10, 1956 in Kazan.

He was born on April 4, 1882 in the town of Irgiz in the Turgai region. He entered the natural sciences department of the physico-mathematical faculty in Kazan University in 1902. During his school years Vasilev had been attracted to chemistry and had been studying it independently. On entering the University he accordingly chose to specialise in chemistry. For the work which he carried out in the faculty on a subject dealing with eutectic mixtures from the viewpoint of interactions of solid materials, the University Council awarded student Vasilev a gold medal.

In 1908 he took the University examination and got first class honors; on Professor F. M. Franko's advice he stayed on at the University to train for professorship. The young scientist started off as a teacher on "Gas Analysis", In the autumn of 1912 he was entrusted with giving the course of "Qualitative Analysis", and, beginning in 1913 he also gave lectures on quantitative analysis. In the autumn of 1917 he was made a lecturer at the University, and starting in 1918 became a professor and headed the laboratory of qualitative and quantitative analysis.

It was Vasilev who was responsible for organizing an independent chair of analytical chemistry in the University; he continued as head of this department till the last days of his life.

In 1930 a Chemico -Technological Institute was organized in Kazan, and Vasilev became a Professor in the Institute and was head of the chair of analytical chemistry, which he also continued to be till his last days.

During his fruitful teaching career, Professor A. M. Vasilev prepared hundreds of young specialists including analytical specialists.

From his work on general and inorganic chemistry one should note an interesting piece of research on "Pyrogenic Catalytic Synthesis of Ammonia" (1918). In the course of this work experiments were carried out on the catalytic action of metallic manganese on the interaction of nitrogen and hydrogen at high temperatures to form ammonia. Actually, this was the first synthesis of ammonia from its elements achieved in our country. Haber's work was unknown to Vasilev at this time.

Of his more recent work, on inorganic chemistry, mention should be made of the articles "Halogen Compounds of Boron and Their Melting Points", and "Structure and Nomenclature of Boron Hydrides". Vasilev returned to this question of the structure of boron hydrides in a more recent work, published in the Jubilee Symposium of Scientific Transactions of Kazan University. One should also mention Vasilev's work "The Solubility of Platinum Black in Hydrochloric Acid", and his work on the preparation of phosphorescent compounds.

He wrote some articles on the history of chemistry: "The Origin of the Names of the Chemical Elements", and "A Brief Survey of the History of Our Information on Gases".

An appreciable amount of his work was devoted to analytical chemistry The first papers by him on analytical chemistry relate to the early years of his scientific activity ["The Use of Nitron in Nitric Acid Analysis" (1910), "Indirect Analysis of the Halides of Antimony and Tin"].

He has suggested quite a few new analytical methods which have found their way into various textbooks on analytical chemistry. In 1932 "A Rapid Method for the Simultaneous Determination of Calcium and Magnesium" was published.

A number of his articles have been devoted to volumetric gas measurements. A gas-volumetric method for determining potassium through the cobaltinitrite, which is based on decomposition of potassium cobaltinitrite by ferrous salts to give nitric oxide, has found application in agrochemical analysis.

One of the basic lines in analytical chemistry along which Vasilev directed his scientific studies was the phenomenon of coprecipitation. He studied the causes of this phenomenon and established methods of preparing pure precipitates. Under his direction studies were carried out on the precipitation of many sparingly soluble materials ($BaSO_4$, $PbSO_4$, CaC_2O_4, etc.) in the presence of various cations and anions, in the analytical chemistry departments of both the Kazan University and Kazan Chemico-Technological Institute.

In his work on coprecipitation, emphasis is laid on the connection between this phenomenon and adsorpti- tion processes which lie at the basis of the chromatographic method. As a result, his interest in chromatography is no accident; he was particularly interested in the use of ion exchange and its application to analytical chemistry. In this field, his work on the separation of PO_4^{3-} from various cations is well-known. In conjuction with coworkers he also published work on quantitative separation of copper, cadmium, and zinc from thiosulfate solutions. Of his work in theoretical chemistry mention must be made of the formula he derived for the extent of neutralization, which gives a relation between the amount of weak acid titrated and its dissociation constant for a given hydrogen ion concentration. His formula allows one, with a normal degree of accuracy, to make some conclusions which are of interest in volumetric analysis.

He never divorced theory from practice. Vasilev insisted on the necessity for developing an independent theory of analytical chemistry. "Before undertaking any scientific research in analytical chemistry", said Vasilev, "there is the problem of finding out how to direct the reactions being used, and how to use all the sum total of knowledge which science has worked out". He welcomed new research methods and set his pupils the task of using them. Under his direction numerous studies were made of the stability of complexes by the polarographic method, and on the application of polarographic and amperometric methods in analysis.

He payed a lot of attention to the use of organic reagents in analytical chemistry; he wrote a very good review of this field, which was published in the Transactions of the Commission on Analytical Chemistry in 1947.

He also gave a lot of his attention to the training of scientific personnel; under his immediate direction more than 20 theses were submitted on analytical chemistry. His scientific activity was not confined within the walls of the University and Institute laboratories. He acted as a consultant on analytical chemistry for many factories. He was a member of the Commission of Analytical Chemistry of the USSR Academy of Sciences, and always took part in All-Union Conferences on analytical chemistry. He was a member for many years of the Presidium of the Kazan branch of the Mendeleev All-Union Chemical Society, and took an active part in its work.

He published a number of articles on questions relating to the teaching of analytical chemistry, and read reports on several occasions at conferences. Vasilev's "Collection of Problems in Analytical Chemistry" is a valuable textbook for teachers and students.

In 1940, in connection with the 10th anniversary of Kazan Chemico-Technological Institute, and the 50th anniversary of industrial education in Kazan, The Presidium of the Supreme Soviet of the TASSR decorated Vasilev. In 1947 he was given a further decoration. He has also been awarded the Order of Lenin, the Order of the Red Banner, and a medal for "Glorious Service in the Great War". His inevitable death has stopped the varied activities of Vasilev who devoted himself to the service of science and the education of a young generation of chemists. He will always be remembered by his numerous students, coworkers, and all who knew him as a great scientist, a sympathetic teacher, and a fine man.

BLANK
PAGE

FROM THE CHEMICAL NOMENCLATURE COMMISSION OF THE DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE U S S R

The Division of Chemical Sciences of the Academy of Sciences of the USSR has set up a Chemical Nomenclature Commission, and this body collects and studies material in various languages on the nomenclature of organic and inorganic compounds with a view to the development of scientific nomenclatures for chemical compounds in the various languages of the peoples of the USSR and their introduction into practice.

The Commission is now working on several schemes of nomenclature, and it is intended to publish these, so that they may be discussed at a conference representing a wide range of interests. This conference is to be held by the Division of Chemical Sciences in the first quarter of 1957, and it is desirable that it should be preceded by extensive informal discussion of the projected schemes.

Among documents of cardinal importance, the Commission has received:

A. Documents on the nomenclature of organic compounds

1) The 1892 Geneva rules and modifications of these introduced in the fourth edition of Beilstein's Handbuch. 2) Rules adopted by the International Union of Pure and Applied Chemistry during 1930-1953. 3) Scheme for the systematic naming of organic compounds in Russian. 4) Scheme for the systematic nomenclature of hydrocarbons and fundamental heterocyclic nuclei (International Union of Pure and Applied Chemistry, 1955). 5) New proposals of Dyson, Taylor, and Patterson for the naming of polycyclic structures (1955).

B. Documents on the nomenclature of inorganic compounds

1) Material discussed by the Nomenclature Commissions of Mendeleev Congresses, compiled by A.Kh. Bork. 2) Rules of the International Union of Pure and Applied Chemistry.

The first three items of Group A were published in "Nomenclature of Organic Compounds" by A.P. Terentyev and others (Acad. Sci. USSR Press, Moscow, 1955). For the first item of Group B see Progr. Chem. 6, 605-621 (in which a detailed bibliography is given), 924, 1251, 1732 (1937). The rest of the material will be published by the Commission.

The Commission invites industrial organizations, research institutes, higher-education establishments, publishers of books and journals, and individual chemists to send in suggestions and comments on matters relating to the nomenclature of organic and inorganic compounds.

Correspondence should be addressed to the Nomenclature Commission, Division of Chemical Sciences, 14 Bolshaya Kaluzhskaya, Moscow, or direct to the chairman of the Commission, A.P. Terentyev, Corresponding Member of the Academy of Sciences of the USSR (Moscow B-234, Chemistry Department, Moscow State University).

Recommendations of the Commission

The Commission recommends that, for Russian publications and for teaching conducted in the Russian language, the names and symbols used for the chemical elements should be those given in the official table (below). This table gives also the values of atomic weights confirmed by the International Commission on Atomic Weights in 1953 and remaining valid for 1956 [Union internationale de Chemie pure et appliquee, Comptes rendus de la XVII Conference. J Am. Chem. Soc. 76, 2033 (1954)].

For some radioactive elements, the mass number of the most stable isotope is given (in square brackets),

TABLE OF THE RUSSIAN NAMES AND SYMBOLS OF THE CHEMICAL ELEMENTS

Name	Symbol	Atomic number	Atomic weight	Name	Symbol	Atomic number	Atomic weight
Azot	N	7	14.008	Neon	Ne	10	20.183
Aktinii	Ac	89	227	Neptunii	Np	93	[237]
Alyuminii	Al	13	26.98	Nikel	Ni	28	58.69
Ameritsii	Am	95	[243]	Niobii	Nb	41	92.91
Argon	Ar	18	39.944	Olovo	Sn	50	118.70
Astatii	At	85	[210]	Osmii	Os	76	190.2
Barii	Ba	56	137.36	Palladii	Pd	46	106.7
Berillii	Be	4	9.013	Platina	Pt	78	195.23
Berklii	Bk	97	[249]	Plutonii	Pu	94	[242]
Bor	B	5	10.82	Polonii	Po	84	210
Brom	Br	35	79.916	Prazeodim	Pr	59	140.92
Vanadii	V	23	50.95	Prometii	Pm	61	[145]
Vismut	Bi	83	209.00	Protaktinii	Pa	91	231
Vodorod	H	1	1.0080	Radii	Ra	88	226.05
Volfram	W	74	183.92	Radon	Rn	86	222
Gadolini	Gd	64	156.9	Renii	Re	75	186.31
Gallii	Ga	31	69.72	Rodii	Rh	45	102.91
Gafnii	Hf	72	178.6	Rtut	Hg	80	200.61
Gelii	He	2	4.003	Rubidii	Rb	37	85.48
Germanii	Ge	32	72.60	Rutenii	Ru	44	101.1
Golmii	Ho	67	164.94	Samarii	Sm	62	150.43
Disprozii	Dy	66	162.46	Svinets	Pb	82	207.21
Evropii	Eu	63	152.0	Selen	Se	34	78.96
Zhelezo	Fe	26	55.85	Sera	S	16	32.066
Zoloto	Au	79	197.0	Serebro	Ag	47	107.880
Indii	In	49	114.76	Skandii	Sc	21	44.96
Iod	J	53	126.91	Strontii	Sr	38	87.63
Iridii	Ir	77	192.2	Surma	Sb	51	121.76
Itterbii	Yb	70	173.04	Talii	Tl	81	204.39
Ittrii	Y	39	88.92	Tantal	Ta	73	180.95
Kadmii	Cd	48	112.41	Tellur	Te	52	127.61
Kalii	K	19	39.100	Terbii	Tb	65	158.93
Kalifornii	Cf	98	[249]	Tekhnetsii	Tc	43	[99]
Kaltsii	Ca	20	40.08	Titan	Ti	22	47.90
Kislorod	O	8	16	Torii	Th	90	232.05
Kobalt	Co	27	58.94	Tulii	Tu	69	168.94
Kremnii	Si	14	28.09	Uglerod	C	6	12.011
Kripton	Kr	36	83.80	Uran	U	92	238.07
Ksenon	Xe	54	131.3	Fermii	Fm	100	[255]
Kyurii	Cm	96	[245]	Fosfor	P	15	30.975
Lantan	La	57	138.92	Frantsii	Fr	87	[223]
Litii	Li	3	6.940	Ftor	F	9	19.00
Lyutetsii	Lu	71	174.99	Khlor	Cl	17	35.457
Magnii	Mg	12	24.32	Khrom	Cr	24	52.01
Marganets	Mn	25	54.94	Tsezii	Cs	55	132.91
Med'	Cu	29	63.54	Tserii	Ce	58	140.13
Mendeleevii	Md	101	[256]	Tsink	Zn	30	65.38
Molibden	Mo	42	95.95	Tsirkonii	Zr	40	91.22
Myshyak	As	33	74.91	Einshteinii	En	99	[253]
Natrii	Na	11	22.991	Erbii	Er	68	167.2
Neodim	Nd	60	144.27				

Publisher's Note: The symbols are as in the original; the names are transliterated. The Consultants Bureau convention of transliterating the Russian letters "ий" as "y" at the end of a word has not been followed in this translation.

instead of the atomic weight. These values are derived from data available in the literature on January 1, 1956. Some values confirmed by the International Commission have been altered as follows.

Berkili (berkelium). Previous value 245, half-life 4.95 days. Recommended value 249, half-life 290 days. This is adopted on the basis of the data of Diamond, Magnusson, et al. [Phys. Rev. 94, 1083 (1953); 96, 1576 (1953)].

Kalifornii (califorornium). Previous value 248, half-life 250 days. Recommended value 249, half-life 470 ± 100 years. This is adopted on the basis of the data of Diamond, Magnusson, et al. [Phys. Rev. 94, 1083 (1953); 96, 1576 (1953)].

The table gives also elements No. 99, 100, and 101, which were obtained in 1951-1955 by Seaborg and others. These investigators proposed the names: No. 99, einshteinii (einsteinium, E); No. 100, fermii (fermium, Fm); No. 101, mendeleevii (mendelevium, Mv) [Phys. Rev. 98, 1518 (1955); Progr. Chem. 25, 133 (1956)].

While accepting these names, the Commission recommends the symbol En for einshteinii (einsteinium) and Md for mendeleevii (mendelevium), in accordance with traditional practice for the derivation of the symbols of the elements.

For isotopes occurring in natural radioactive series – as also for the isotopes of other elements – it is recommended that obsolescent historical names should no longer be used: the symbols given in the official list should be used, and the mass number of the isotope should be indicated by an index.

For isotopes of hydrogen and radon (No. 86) it is permissible to use the following names and symbols when necessary, in addition to those recommended: deiterii (deuterium) D; tritii (tritium) T; aktinon (actinon) An; toron (thoron) Tn.

BLANK
PAGE

DIALKYL-AND DIARYLDITHIOPHOSPHORIC ACIDS AS ANALYTICAL REAGENTS

PART 1. POTENTIOMETRIC DETERMINATION OF COPPER BY MEANS OF NICKEL DIETHYLDITHIOPHOSPHATE

A. I. Busev and M. I. Ivanyutin

The M. V. Lomonosov Moscow State University

The use of diethyldithiophosphoric acid $(C_2H_5O)_2PSSH$ as an analytical reagent was suggested in 1949 [1-3]. Small amounts of molybdenum can be detected in the presence of tungsten, vanadium, uranium, titanium, and other elements [1, 2], on the basis of the formation of an inner complex compound which has an intense raspberry color, when molybdenum reacts with diethyldithiophosphoric acid. The acid can be used for complexing ruthenium during detection of osmium by thiourea [3].

Diethyldithiophosphoric acid, as well as other dialkyl- and diaryldithiophosphoric acids, is undoubtedly worthy of further systematic study as analytical reagent. The presence in the molecule of the sulfhydryl group, SH, whose hydrogen, obviously can be replaced by a metal, as well as the S and O atoms, determine the capacity of these reagents to give inner complex compounds with a number of elements which are of interest for analytical chemistry.

Diethyldithiophosphoric acid precipitates (quantitatively) from neutral or weakly acid solutions, the ions of many heavy metals (Hg^{2+}, Ag^{+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, Pd^{2+}, Pt^{II}, Ir^{III}, Rh^{III}, Pb^{2+}) (white or yellow precipitates), and gives colored compounds with some ions (Mo, Re). The following ions (under all test conditions studied)* are not precipitated: those of the alkali and alkaline earth elements, Al^{3+}, Zn^{2+}, Mg^{2+}, Ge^{IV}, Cr^{III}, Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}, Ga^{3+}, Be^{2+}, Ti^{IV}, Zr^{IV}, V^{V}, U^{VI}. Tl^{+} and In^{3+} (the latter at a pH of 2.0-3.2) are partially precipitated. By using complexing agents and regulating the pH, the selectivity of diethyldithiophosphoric acid as a precipitant can be increased considerably. By comparing the results adduced in Table 1, one can note the possibilities of separating a number of combinations of elements of analytical interest.

The solubility of sparingly soluble diethyldithiophosphates increased in the following sequence: **

$$HgR_2,\ AgR,\ BiR_3,\ PbR_2,\ CdR_2,\ TlR\ [R = (C_2H_5O)_2PSS-].$$

The freshly precipitated diethyldithiophosphates of some metals dissolve readily in organic solvents which are immiscible with water.

Since the diethyldithiophosphates of divalent mercury and silver are least soluble (of the diethyldithiophosphates tested), one would expect that metallic mercury and silver would be suitable electrodes during titration of the ions of some metals with a solution of diethyldithiophosphoric acid:

$$Hg|\ HgR_2||R^-;\ Ag\ |\ AgR||R^-.$$

7

Experiment showed that the potential of the mercury or silver is dependent on the concentration of the anion of diethyldithiophosphoric acid in solution. During titration of solutions of salts of some heavy metals with a solution of diethyldithiophosphoric acid, or with a solution of its soluble salt, on a silver or platinum electrode covered with electrolytic mercury, a potential jump can be observed at a certain point. This gives one a basis for using the potentiometric method for studying precipitation reactions, and for developing a potentiometric method for determining individual elements.

---

*Nickel and cobalt give colored precipitates if solid $NiSO_4 \cdot 7H_2O$ or $CoSO_4 \cdot 7H_2O$ respectively, are added to a comparatively concentrated solution of diethyldithiophosphoric acid to the point of saturation.

**The formulas given for the compounds formed are hypothetical.

TABLE 1

Precipitation of Metal Ions with Diethyldithiophosphoric Acid Under Varying Conditions

Medium	Element																		
	Mo	Re	Sn^{II}	Sb^{III}	As^{III}	As^{V}	SeO_3^{2-}	TeO_3^{2-}	Hg^{2+}	Ag	Pb	Bi	Cd	Cu^{II}	Tl^{I}	In^{III}	Fe^{III}	Pd	Pt
Weak hydrochloric acid solution (pH 1)	±		+	+	+	−	+	+	+	+	+	+	+	+	±	±	±	+	+
Weak HCl solution + excess NaF (pH 1)	±		+	±	±	−	+		+	+			+	+	±	−	−	+	
Weak acid solution + excess $CS(NH_2)_2$ (pH 1)	±			+	+	+			+	−		+	−	+		±			
HCl (1:1)	+		+	+	+	+	+	+	+			+	−	+		−	+	+	
$NaHC_4H_4O_6$ solution + NH_3 up to pH ~ 9	−	−	−	−	−	−	−	−	+	+	+	−	−	+	±	+	−	+	−
$NaHC_4H_4O_6$ (excess) + NH_3 up to pH ~ 13	−		−	−	−	−			+	+	−	−	−	−	±	−	−		
$NaHC_4H_4O_6$ (excess) + Na_2CO_3 to pH ~ 9 + KCN	−		−	−	−	−	−		−	−		±	--	−	±	−	−	−	
Trilon B solution (excess) + NH_3 to pH ~ 9	−		−		−	−			+	+	−	−	−	−	±	−		+	−
Concentrated NH_3 in a ratio of 1:1	−				−	−			±	±			−	−					

Designations: + precipitate forms; − precipitate does not form; ± precipitate only formed at comparatively high ionic concentration.

The present article is devoted to the study of the reaction between divalent copper and the nickel salt of diethyldithiophosphoric acid, and to the development of a potentiometric method for determining copper in a number of alloys and ores.

EXPERIMENTAL

a) Synthesis of Nickel Diethyldithiophosphate. The phosphorus pentasulfide necessary for this synthesis is prepared by careful fusion of sulfur and phosphorus in stoichiometric proportions. To 252 g of finely ground phosphorus pentasulfide contained in a large conical flask is added 255 ml of 96% ethyl alcohol. The reaction starts at room temperature with evolution of hydrogen sulfide; the reaction gradually speeds up with simultaneous spontaneous heating up and copious evolution of hydrogen sulfude; it reaches a maximum and then after a certain time interval dies down. If the flask taken is not large enough, some of the reaction mixture may overflow (this can be prevented by gradual addition of alcohol). When the intensity of the reaction has decreased, the contents of the flask are carefully heated; evolution of gas then increases. The reaction mass is then left to stand overnight. The black oily liquid which has a strong odor is filtered, the sulfurous residue (S, etc.) is thrown away. Double its own volume of water is added to the filtrate and the whole vigorously mixed; it is then left to separate into layers; the somewhat turbid aqueous layer is separated, centrifuged and filtered through filter paper. In order to get a more complete extraction of diethyldithiophosphoric acid, a fresh lot of water is added to the oily layer and the whole sequence of operations repeated. Usually, after three water treatments, the aqueous phase gives only a weak red color with a strong hydrochloric acid solution of ammonium molybdate. The oily liquid is thrown away. To the clear aqueous solution of diethyldithiophosphoric acid ground up nickel sulfate is added to the saturation point. When this is done violet crystals of nickel diethyldithiophosphate separate out. The crystals are filtered off under suction, and dried on filter paper. The yield of crude product is 207 g. For further purification, 47 g of nickel diethyldithiophosphate is dissolved in 190 ml of acetone and the solution obtained, filtered (small amounts of nickel sulfate are retained on the filter). To the filtrate is added 200 ml of water with adequate stirring. Crystals of nickel diethyldithiophosphate separate out immediately, and are filtered off under suction. Forty grams of air-dried material is obtained in this way. The melting point is 105° (this agrees with the published value of 105° [4]). The preparation has a weak odor. The crude product can also be pruified by recrystallization from ethyl acetate. The melting point of the final product when this variant is used is 104-105°. Other organic solvents are less suitable on account of the very high solubility of nickel diethyldithiophosphate in them.

The value found for nickel when the latter was determined by the dimethylglyoxime method was 13.47%. The theoretical nickel content for $[(C_2H_5O)_2PSS]_2Ni$ should be 13.70%.

b) Preparation of Standard Solutions of Nickel Diethyldithiophosphate and Cupric Sulfate. The composition of nickel diethyldithiophosphate, within the limits of experimental error, corresponds to the formula $[(C_2H_5O)_2PSS]_2Ni$; the salt does not contain any water of crystallization and it not hygroscopic; it is completely stable on keeping. Accordingly, standard solutions of $[(C_2H_5O)_2PSS]_2Ni$ (0.05 N or 0.1 N) can be prepared by dissolving an exact amount of the pure preparation in water in a standard flask. Its normality remains constant for approximately one week. Its strength should be checked periodically, iodometrically.

In this connection a detailed study was made of the oxidation of the anion of diethyldithiophosphoric acid by iodine under various conditions (various acids at different concentrations). For purposes of calculation it is assumed that the gram-equivalent of nickel diethyldithiophosphate is equal to half the molecular weight (i. e. 214.5). The results given in Table 2 show that changes in concentration of H_2SO_4 or HCl, over a wide range, have practically no effect on the accuracy of determination of $[(C_2H_5O)_2PSS]_2Ni$ during titration with I_2 solution. Even at comparatively high concentrations of HCl and H_2SO_4, when there is a chance of oxidation of the I ion to I_2 by atmospheric oxygen, completely satisfactory results are obtained. During titration of $[(C_2H_5O)_2PSS]_2Ni$ with I_2 solution in the presence of concentrated HCl (after standing for 2 hours) somewhat low results are obtained. If titration is carried out immediately in the presence of concentrated HCl (addition of 20 ml of concentrated HCl to 10 ml of $[(C_2H_5O)_2PSS]_2Ni$, it is still possible to get satisfactory results.

TABLE 2

Titration of $[(C_2H_5O)_2PSS]_2Ni$ with I_2

Amount of $[(C_2H_5O)_2PSS]_2Ni$ taken in g	Acid added in ml		I_2 solution used in ml (N — 0,08223)	$[(C_2H_5O)_2PSS]_2Ni$ found in g	Error in %
0.1980	No acid added		11.20	0.1976	—0.02
0.1121	2 *N* HCl	20	6.40	0.1127	+0.06
0.1049	2 *N* HCl	20	6.0	0.1057	+0.8
0.1097	2 *N* HCl	20	6.35	0.1199	+0.2
0.1066	2 *N* H_2SO_4	10	6.10	0.1074	+0.8
0.0984	2 *N* H_2SO_4	10	5.60	0.0987	+0.3
0.1251	2 *N* H_2SO_4	10	7.10	0.1252	0
0.2008	2 *N* H_2SO_4	20	11.50	0.2028	+1
0.1913	2 *N* H_2SO_4	20	10.90	0.1922	+0.4
0.2125	2 *N* H_2SO_4	20	12.10	0.2133	+0.3

The results obtained showed that the reaction between $[(C_2H_5O)_2PSS]_2Ni$ and I_2 is strictly stoichiometric under certain conditions:

$$[(C_2H_5O)_2PSS]_2Ni + I_2 = (C_2H_5O)_2PSS - SSP(OC_2H_5)_2 + NiI_2.$$

No side reactions are observed. Nickel diethyldithiophosphate reacts with iodine at room temperature very rapidly, even at the equivalence point, when the concentration of $[(C_2H_5O)_2PSS]_2Ni$ is low. The equivalence point can readily be observed by bluing of starch on adding one drop of iodine in excess. The iodometric method therefore ensures that the results obtained during checking of the normality of $[(C_2H_5O)_2PSS]_2Ni$ are completely reliable.

Cupric sulfate solutions are also standardized iodometrically.

c) Apparatus. Experimental Procedure. A MOSKIP P-3 potentiometer was used. A platinum wire covered with electrolytic metallic mercury [from a nitric acid solution of $Hg_2(NO_3)_2$] and fused into a glass tube was used as indicator electrode. The electrode can be used for 3-5, sometimes even more, titrations. After each titration, the electrode was washed with CCl_4, dilute HNO_3, and water. A saturated calomel electrode was used as the reference electrode. The solution being titrated was stirred with a mechanical stirrer.

Study of the Reaction Between Cu^{2+} Ions and $[(C_2H_5O)_2PSS]_2Ni$*

The curve obtained during potentiometric titration of a solution of a copper salt with $[(C_2H_5O)_2PSS]_2Ni$, using a mercury indicator electrode, has the usual form. A sharp jump in the potential of the indicator electrode is observed for a molar ratio of $CuSO_4$ to $[(C_2H_5O)_2PSS]_2Ni$ close to unity (Table 3). During titration of Cu^{2+} ions in a tartrate solution at a pH of 8 with a solution of $[(C_2H_5O)_2PSS]_2Ni$, the equivalence point is also found at a ratio of $Cu^{2+} : NiR_2 = 1.001$.

On addition to the solution being titrated of approximately an equal volume of CCl_4, the potential jump at the equivalence point drops sharply and sometimes cannot even be observed at all. This can be explained by the fact that excess reagent is readily extracted by CCl_4 (just like copper diethyldithiophosphate). Accordingly, the interaction proceeds according to the following equation:

$$CuSO_4 + [(C_2H_5O)_2PSS]_2Ni = [(C_2H_5O)_2PSS]_2Cu + NiSO_4.$$

During titration a change in the color of the precipitate is observed. It is possible that this is connected with the subsequent reduction of divalent copper to the univalent state by diethyldithiophosphate anions according to the equation:

$$2[(C_2H_5O)_2PSS]_2Cu = [(C_2H_5O)_2PSS]_2Cu_2 + [(C_2H_5O)_2PSS]_2.$$

Adding up the two equations, we get:

$$\begin{array}{c} 2CuSO_4 + 2[(C_2H_5O)_2PSS]_2Ni = 2[(C_2H_5O)_2PSS]_2Cu + 2NiSO_4 \\ 2[(C_2H_5O)_2PSS]_2Cu = [(C_2H_5O)_2PSS]_2Cu_2 + [(C_2H_5O)_2PSS]_2 \\ \hline 2CuSO_4 + 2[(C_2H_5O)QSS]_2Ni = [(C_2H_5O)_2PSS]_2Cu_2 + [(C_2H_5O)_2PSS] + NiSO_4 \end{array}$$

It is obvious that the molar ratio between $CuSO_4$ and $[(C_2H_5O)_2PSS]_2Ni$ is preserved. The gram-equivalent of copper is equal to half the atomic weight (31.78).

Amounts of zinc, magnesium, aluminum, and divalent iron, as well as hydrochloric, orthophosphoric, and nitric acids (Table 4), considerably in excess of the Cu^{2+} ion have practically no effect on the titration of the latter. Divalent tin interferes. Accordingly, if determination has to be carried out in the presence of tin, the tin should be oxidized beforehand to the tetravalent state. Tetravalent tin, even in large excess has no observable effect on copper determination. Ferric iron should be absent, since it oxidizes (comparatively slowly) diethyldithiophosphoric acid to the disulfide. Traces of ferric iron however do not lead to appreciable errors. It should be pointed out, that as qualitative tests showed, the black compoind of ferric iron with diethyldithiophosphoric acid in acid media, on addition of a solution of Cu^{2+} ions, is converted practically quantitatively and very rapidly to copper diethyldithiophosphate; this fact is readily observed by the disappearance of the black color, and the appearance of the characteristic color of the copper diethyldithiophophate.

When the Fe^{3+} ion in a weakly acid solution is complexed by addition of orthophosphoric acid, it has no effect on titration of copper. Attempts to eliminate the effect of divalent tin and trivalent iron by carrying out titrations in alkali solutions were unsuccessful.

---

*V. K. Akimov took part in this study.

TABLE 3

Stoichiometric Ratios Between $[(C_2H_5O)_2PSS]_2Ni$ and $CuSO_4$
In each test 10.00 ml of $CuSO_4$ containing 0.7603 millimole Cu was taken

Used $_{[(C_2H_5O)_2PSS]_2Ni}$			M_{Cu}
ml	$T_{[(C_2H_5O)_2PSS]_2Ni}$	millimole	$M_{[(C_2H_5O)_2PSS]_2Ni}$
33.40	0.01002	0.7774	0.977
29.60	0.01111	0.7660	1.025
29.30	0.01111	0.7590	1.01
29.25	0.01111	0.7570	1.004
		Mean	1.004

TABLE 4

Effect of Other Metals on the Accuracy of Titration of Copper with a Solution of $[(C_2H_5O)_2PSS]_2Ni$
In each test 0.0483 g of Cu as $CuSO_4$ was taken (initial volume 10 ml)

Material added	Used $[(C_2H_5)_2PSS]_2Ni$		Cu found in g	Absolute errir in g
	in ml	N		
—	29.25	0.05178	0.0481	−0.0002
—	29.30	0.05178	0.0482	−0.0001
1 g $ZnSO_4 \cdot 7H_2O$	29.25	0.05178	0.0481	−0.0002
$MgSO_4 \cdot 7H_2O$	27.25	0.05655	0.0490	+0.0007
5 ml 2N + 1g $AlCl_3$	33.35	0.04566	0.0484	+0.0001
5 ml conc. H_3PO_4	33.45	0.04566	0.0485	+0.0002
5 ml conc. H_3PO_4 + 1 g $FeCl_3$	33.50	0.04566	0.0486	+0.0003
5 ml conc H_3PO_4 + 1 g $FeCl_3$	33.45	0.04566	0.0485	+0.0002
5 ml conc. HNO_3	33.45	0.04566	0.0485	+0.0002

Determination of Copper

Precipitation of Cu^{2+} satisfies all the requirements of the potentiometric method, while at the same time it is comparatively selective. This permits one to develop simple methods of determining copper in iron-manganese brass, beryllium and silicon-nickel bronze, tombac, copper sulfide, and oxide ores.

An aliquot of the alloy or of the ore dried at 105° is dissolved in dilute HCl, HNO_3, or H_2SO_4; nitrogen oxides are removed by boiling (if HNO_3 has been used) and the Cu^{2+} ions titrated with a solution of $[(C_2H_5O)_2PSS]_2Ni$ the mercury electrode gives an indication of a potential jump. Any silicic acid contained in the ores is not filtered off.

The method gives completely satisfactory results (Table 5).

During the analysis of Muntz brass containing 60.40% Cu, 38.65% Zn, 0.92% Pb

Interference on the part of lead can be eliminated by precipitating it as the sulfate in the standard flask in which the solution to be analyzed is prepared. The clear, supernatant liquid is taken for analysis. We showed experimentally that this technique enables copper to be determined in the presence of large amounts of lead.

TABLE 5

Determination of Copper in Various Technical Materials

Alloy or ore	Cu in %	Weight of sample in g	Used $[(C_2H_5O)_2PSS]_2Ni$		Cu found in %	Absolute error in %
			ml	N		
Iron-manganese brass: Zn 37.68; Fe 0.945; Mn 0.70; Al 0.13; Sn 0.66; Pb 0.050	59.84	0.04128	17.75	0.04396	60.09	0.25
Beryllium bronze: Be 2.12; Fe 0.175; P 0.011; Mg 0.0.8; Al 0.04; Ni 0.18; Sn 0.12; Pb 0.003 . . .	97.26	0.02199	15.30	0.04396	97.16	0.10
Tompac Zn 10.17; Fe 0.16 .	89.63	0.04055	25.60	0.04465	89.59	0.03
Silicon-nickel bronze: Si 0,98; Ni 3.18; Mn 0.34; Fe 0.054; PO 0.003; Sn 0.022; Zn 0.035 . . .	95.39	0.04106	27.65	0.04465	95.60	0.21
Copper oxide ore	2.83	—	—	—	2.82	0.01
Copper sulfide ore	2.80	—	—	—	2.75	0.05

SUMMARY

The reaction which occurs between divalent copper and nickel diethyldithiophosphate has been studied, and a method has been developed for determining copper in a number of alloys and ores.

Received September 19, 1955

LITERATURE CITED

[1] A. I. Busev, J. Anal. Chem. 4, 4, 234 (1949).

[2] A. I. Busev, Proc. Acad. Sci. 66, 6, 1093 (1949).

[3] A. I. Busev, J. Anal. Chem. 4, 1, 49 (1949).

[4] L. Malatesta, and R. Pizzotti, Chimia e industria 27, No. 1-2, 6 (1945).

THE SOLUBILITY PRODUCTS OF A NUMBER OF ARSENATES

V. G. Chukhlantsev

The S. M. Kirov Ural Polytechnical Institute, Sverdlovsk

A knowledge of the solubility of arsenates is of great importance both from an analytical point of view, and also for the purpose of developing arsenic-containing materials. The only published material relates to the solubility of silver arsenate [1]. Whitby found that at 20° the solubility of silver arsenate is $8.5 \cdot 10^{-4}$%. The solubility product calculated on the basis of this result is $3.1 \cdot 10^{-18}$. In the work described in the present article, the solubility products of the arsenates of the following metals were determined – mercury, manganese, lead, cobalt, nickel, aluminum, chromium, iron, and bismuth; they were all prepared from chemically pure reagents.

Preparation of the Arsenates

Mercury Arsenate. Five grams of mercurous nitrate was dissolved in 50 ml of water and acidified with nitric acid (1 ml of concentrated nitric acid was added). The solution was heated to 50-60° and a solution containing 5 g of arsenic acid added dropwise. The precipitate formed was left in the mother liquor for 24 hours, the liquid removed by centrifuge, and the precipitate finally dried at 40°. Mercury was determined volumetrically with ammonium thiocyanate. Arsenic was determined bromatometrically after preliminary separation from mercury. The gram-ion ratio of mercury to arsenate was found to be 3.02.

Manganese Arsenate. Concentrated solutions of sodium arsenate and manganese sulfate were poured together in stoichiometric proportion. The precipitate was kept for a long time in the mother liquor at an elevated temperature, the water then removed by centrifuging, and the precipitate dried at 70°. Manganese was determined gravimetrically as manganous sulfate. Arsenic was distilled off in hydrochloric acid solution after reduction, and then determined volumetrically. The gram-ion ratio of manganese to arsenate in this case was 3:2.02.

Lead Arsenate. 0.1 N lead acetate and sodium arsenate solutions were poured together in stoichiometric proportions at 60°. The lead acetate solution contained free acetic acid in an amount of 20 g/liter. The dense white precipitate was filtered, washed with water, and dried at 50°. Lead was determined gravimetrically as the sulfate, arsenic – volumetrically by means of potassium bromate. The gram-ion ratio of lead to arsenate was fount to be 1.51.

Cobalt Arsenate. On pouring together 0.5 N solutions of cobalt nitrate and sodium arsenate, taken in stoichiometric proportions, an amorphous violet precipitate was formed. The temperature of the solutions was 50-60°. The precipitate was left in the mother liquor for a few days, water removed by centrifuging and the precipitate dried at 60°. Cobalt was determined gravimetrically as the sulfate, arsenic – volumetrically after reduction to the trivalent state. The gram-ion ratio of cobalt to arsenate was 1.51.

Nickel Arsenate. Nickel arsenate was prepared in the same way as cobalt arsenate. The green amorphous precipitate was separated by centrifuging and dried at 40°. Nickel was determined gravimetrically, after precipitation with dimethylglyoxime, while arsenic was determined volumetrically by titration with potassium bromate. The gram-ion ratio of nickel to arsenate was 1.49.

Aluminum Arsenate. On pouring together dilute solutions of aluminum sulfate and sodium arsenate, as a rule a basic aluminum arsenate was obtained. The neutral salt was obtained on heating a saturated solution of aluminum sulfate with sodium arsenate under pressure. Arsenic was distilled off with hydrochloric acid after reduction with hydrazine, and then determined in the distillate volumetrically. Aluminum was determined in the residue gravimetrically. The gram-ion ratio of aluminum to arsenate was 1.03.

Chromium Arsenate. 0.5 N solution of potassium arsenate and 1 N chromium sulfate solution were poured together in proportions suitable for preparing the neutral salt. The temperature of the solutions was 50-60°. The dark green precipitate was kept for some days in the mother liquor, water then removed by centrifuging, and the precipitate dried at 50°. Chromium was determined gravimetrically and colorimetrically, while arsenic was determined volumetrically by means of potassium bromate. The gram-ion ratio of aluminum to arsenate was 0.99.

Ferric Arsenate. Heated 0.1 N solutions of ferric sulfate and sodium arsenate were poured together in stoichiometric proportions. Sodium sulfate was added to the suspension obtained to improve coagulation of the precipitate. The precipitate was kept in the mother liquor for 24 hours, water removed by centrifuging, and the precipitate dried at 60°. Iron was determined gravimetrically after distilling off the arsenic; arsenic was determined in the distillate volumetrically. The gram-ion ratio of iron to arsenate was 1.01.

Bismuth Arsenate. To a 0.1 N sodium arsenate solution was added with stirring a 0.1 N bismuth nitrate solution, and a 0.25 N nitric acid solution, in stoichiometric proportions. The temperature of the solutions was 50-60°. The fine crystalline product was filtered, washed with water, and dried at 50°. Bismuth was determined gravimetrically, and arsenic volumetrically. The gram-ion ratio of bismuth to arsenate was 1:0.99.

Taking into account the fact that the results of chemical analysis only allows one to have an idea of the mean chemical composition of the precipitate, the precipitates were examined during precipitation of the arsenates. With this aim in view we added various amounts of arsenate to equal portions respectively of solutions of the salts of mercury, lead, cobalt, nickel, chromium, bismuth, of known concentrations. The concentration of arsenate was determined accurately. When these solutions were added together, precipitation occurred; the residual concentration of cations was then determined in the liquid phase. It was shown experimentally that the composition of the respective precipitates did not change in the presence of excess arsenate ions. As examples of the results obtained we adduce curves for the arsenates of lead, cobalt, chromium, and bismuth. The amounts of added arsenate ions in gram-ions are plotted along the abscissa in the diagrams, while along the ordinate the corresponding residual content of the cation is plotted. These experiments confirmed the correctness of chemical analysis of the respective compositions.

Determination of the Solubility of the Arsenates and Calculation of Solubility Product

The solubility of the arsenates was studied in dilute nitric, hydrochloric, and sulfuric acids respectively. The water used for preparing the solutions was twice distilled and freed from carbon dioxide. Calculations of solubility products were carried out on the basis of a method suggested by Babko for precipitates dissolved in acids [2]. This method of calculation was used by Zharovsky for determining the solubility products of the phosphates of a number of metals [3], and by Korenman for determining the solubility products of the oxalates of a series of rare-earth elements [4]. Values obtained for the solubility products of the oxalates as found by the method of labeled atoms, and by the calculation method respectively, are in good agreement. pH was measured on a UNIKhIM pH meter using a glass electrode; the accuracy of measurement was ± 0.05 pH units. pH meter operation was checked by means of standard buffer solutions prepared according to Britton [5].

The exact value of the pH of the buffer solutions was determined potentiometrically by means of the quinhydrone electrode. The absence of data for the activity coefficients of the given system did not allow calculation of the activity product. Flasks containing arsenate and a solution of a definite acidity were placed in a thermostat and shaken for 12 hours. It had been established beforehand that this time was sufficient for equilibrium to be reached. Temperature was maintained constant to an accuracy of ± 0.05°. Hydrogen ion concentration was determined in one part of the saturated solution, while in another part, metal concentration corresponding to the saturated state was determined. The composition of the solid phase did not change during attainment of the saturated state. Best separation of solid and liquid phase was achieved by using ultrafilters.

Small amounts of manganese, iron, and chromium (3-5 mg) were determined colorimetrically on an "FEK-M" type photocolorimeter. Mercury was determined volumetrically by titration with 0.01 N ammonium thiocyanate. Gravimetric methods of analysis were used when large amounts of metals were involved. The methods used were taken for the most part from the book by Hillebrand and Lendel [6]. Results of duplicate experiments agreed with a sufficient degree of accuracy. Deviations from the mean value did not exceed 5%. Arsenate ion concentration was determined from the values of the dissociation constant of arsenic acid, hydrogen ion concentration, and metal ion concentration. The total concentration [S] of the acid, the same as the precipitate is equal to:

$$[S] = [H_3AsO_4] + [H_2AsO_4^-] + [HAsO_4^{2-}] + [AsO_4^{3-}].$$

Having substituted the values of the individual forms of the acid by the corresponding values of $[H^+]$, K_1, K_2 and K_3, we get

$$[S] = \frac{[H^+]^3}{K_1K_2K_3}[AsO_4^{3-}] + \frac{[H^+]^2}{K_2K_3}[AsO_4^{3-}] + \frac{[H^+]}{K_3}[AsO_4^{3-}] + [AsO_4^{3-}] = \left[\frac{[H^+]^3}{K_1K_2K_3} + \frac{[H^+]^2}{K_2K_3} + \frac{[H^+]}{K_3} + 1\right][AsO_4^{3-}].$$

Designating the reciprocal of the expression in brackets by q, we get $[AsO_4^{3-}] = q\,[S]$,

where q is a coefficient whose value changes with hydrogen ion concentration. For convenience in using this formula, Table 1 was compiled for values of $-\log[AsO_4^{3-}]$ and varying pH and for [S] = 1. Published results on the values of the dissociation constants of arsenic acid differ widely from each other [7-13]. The values of the dissociation constants found by Britton and Jackson were used in the given instance [9]. The authors determined, potentiometrically, using a glass electrode, that at 20°, the values of the dissociation constants K_1, K_2, K_3 were equal to $5.62 \cdot 10^{-3}$; $1.7 \cdot 10^{-7}$; $2.9 \cdot 10^{-12}$ respectively. Consequently, at pH 1 the following values are obtained for $-\log[AsO_4^{3-}]$.

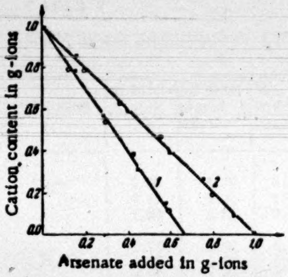


Fig. 1. Change in cation concentration during precipitate formation: 1) lead and cobalt arsenates; 2) chromium and bismuth arsenates; XX) lead, chromium; OO) cobalt, bismuth.

TABLE 1

Values of $-\log[AsO_4^{3-}]$ for [S] = 1 and Various pH's

pH	$-\log[AsO_4^{3-}]$	pH	$-\log[AsO_4^{3-}]$	pH	$-\log[AsO_4^{3-}]$
1	17.57	5	8.32	9	2.53
2	14.74	6	6.27	10	1.54
3	12.37	7	4.73	11	0.65
4	10.31	8	3.55	12	0.13

$$[AsO_4^{3-}] = \frac{K_1K_2K_3}{K_1K_2K_3 + [H^+]K_1K_2 + [H^+]^2K_1 + [H^+]^3} = \frac{2.82 \cdot 10^{-21}}{2.82 \cdot 10^{-21} + 9.56 \cdot 10^{-11} + 5.62 \cdot 10^{-5} + 10^{-3}} = 2.7 \cdot 10^{-18},$$

from which $-$logarithm $[AsO_4^{3-}]$ = 17.57.

To speed up calculation a graph of $-\log[AsO_4^{3-}] = f(pH)$ was compiled from the results of Table 1. pH values were plotted along the ordinate and $-\log[AsO_4^{3-}]$ along the absicissa. Total arsenic acid concentration was determined on the basis of the concentration of the metal ion in saturated solution. For precipitates of the type of $Me_3(AsO_4)_2$, the total concentration of arsenic acid was equal to 2/3 of metal ion concentration. The value of coefficient q was determined from the value of the pH of the saturated solution obtained from the curve $-\log[AsO_4^{3-}] = f(pH)$

$$q = \frac{K_1K_2K_3}{K_1K_2K_3 + [H^+]K_1K_2 + [H^+]^2K_1 + [H^+]^3}.$$

Arsenate ion concentration was found by multiplying coefficient q by the total acid concentration.

The results for solubility product determinations which are given below in the tables, are the mean values of two or more parallel tests.

The mean square error was determined by means of a formula taken from the book by Batuner and Pozin [14].

TABLE 2

Solubility and Solubility Product of Mercury Arsenate at 20°

Solution	pH before shaking	pH of saturated solution	Hg concentration in g-ions/liter	$p[Hg^+]$	pq	$p[AsO_4^{3-}]$	$p[Hg^+]^3 \cdot [AsO_4^{3-}]$
Nitric Acid	2.70	2.80	$3.8 \cdot 10^{-5}$	4.42	12.80	17.70	30.96
	2.20	2.25	$8.3 \cdot 10^{-5}$	4.08	14.05	18.61	30.85
	1.95	2.00	$1.7 \cdot 10^{-4}$	3.77	15.00	19.26	30.56
Sulfuric Acid	2.60	2.65	$5.6 \cdot 10^{-5}$	4.25	13.20	17.93	30.68
	2.20	2.25	$8.9 \cdot 10^{-5}$	4.05	14.05	18.58	30.73
	2.00	2.10	$1.2 \cdot 10^{-4}$	3.92	14.45	18.85	30.61

Mean value $[Hg^+]^3 \cdot [AsO_4^{3-}] \ldots (1.9 \pm 0.6) \cdot 10^{-31}$

TABLE 3

Solubility and Solubility Product of Manganese Arsenate at 21°

Solution	pH before shaking	pH of saturated solution	Mn^{2+} conc. in g-ions per liter	$p[Mn^{2+}]$	pq	$p[AsO_4^{3-}]$	$p[Mn^{2+}]^3 \times [AsO_4^{3-}]^2$
HCl	2.50	4.75	$6.7 \cdot 10^{-3}$	2.17	8.70	11.05	28.61
	2.15	4.20	$1.8 \cdot 10^{-2}$	1.74	9.85	11.77	28.76
	1.90	3.85	$3.5 \cdot 10^{-2}$	1.45	10.55	12.18	28.71
H_2SO_4	2.70	6.00	$4.1 \cdot 10^{-3}$	2.39	8.30	10.86	28.89
	2.20	4.25	$1.5 \cdot 10^{-2}$	1.82	9.70	11.70	28.86
	2.00	4.00	$3.1 \cdot 10^{-2}$	1.51	10.30	11.99	28.51

Mean value $[Mn^{2+}]^3 \cdot [AsO_4^{3-}]^2 \ldots (1.9 \pm 0.7) \cdot 10^{-29}$

TABLE 4

Solubility and Solubility Product of Lead Arsenate at 21°

Solution	pH before shaking	pH of saturated solution	Pb^{2+} conc. in g-ions per liter	$p[Mn^{2+}]$	pq	$p[AsO_4^{3-}]$	$p[Mn^{2+}]^3 \times [AsO_4^{3-}]^2$
Nitric Acid	3.25	4.60	$2.2 \cdot 10^{-4}$	3.66	8.95	12.78	36.54
	2.70	3.80	$1.5 \cdot 10^{-3}$	2.81	10.65	13.64	35.71
	2.20	3.20	$5.9 \cdot 10^{-3}$	2.23	11.85	14.26	35.21
	2.00	3.05	$8.6 \cdot 10^{-3}$	2.07	12.20	14.44	35.09

Mean value $[Pb^{2+}]^3 \cdot [AsO_4^{3-}]^2 \ldots (4.1 \pm 3.6) \cdot 10^{-36}$

TABLE 5

Solubility and Solubility Product of Cobalt Arsenate at 20°

Solution	pH before shaking	pH of saturated solution	Co^{2+} conc. in g-ions per liter	$p[Co^{2+}]$	pq	$p[AsO_4^{3-}]$	$p[Co^{2+}]^3 \times [AsO_4^{3-}]^2$
Nitric Acid	2.15	4.70	$9.8 \cdot 10^{-3}$	2.01	8.80	10.99	28.01
	2.30	5.00	$6.5 \cdot 10^{-3}$	2.19	8.30	10.66	27.89
	1.90	4.30	$1.8 \cdot 10^{-2}$	1.75	9.65	11.57	28.39
Sulfuric Acid	2.40	5.10	$4.1 \cdot 10^{-3}$	2.39	8.00	10.57	28.31
	2.10	4.60	$1.2 \cdot 10^{-2}$	1.92	9.00	11.10	27.96
	1.90	4.20	$2.0 \cdot 10^{-2}$	1.70	9.85	11.73	28.56

Mean value $[Co^{2+}]^3 \cdot [AsO_4^{3-}]^2 \ldots (7.6 \pm 4.2) \cdot 10^{-29}$

TABLE 6

Solubility and Solubility Product of Nickel Arsenate at 20°

Solution	pH before shaking	pH of saturated solution	Ni^{2+} conc. in g-ions per liter	$p[Ni^{2+}]$	pq	$p[AsO_4^{3-}]$	$p[Ni^{2+}]^3 \times [AsO_4^{3-}]^2$
Nitric Acid	2.75	7.00	$8.9 \cdot 10^{-4}$	3.05	4.75	7.98	25.11
	2.30	5.80	$4.1 \cdot 10^{-3}$	2.39	6.70	9.26	25.69
	2.00	5.20	$1.1 \cdot 10^{-2}$	1.96	7.80	9.93	25.74
Sulfuric Acid	2.85	7.10	$6.2 \cdot 10^{-4}$	3.21	4.60	7.98	25.59
	2.40	6.00	$3.4 \cdot 10^{-3}$	2.47	6.30	8.95	25.31
	2.05	5.20	$9.8 \cdot 10^{-3}$	2.01	7.80	9.98	25.99
	1.90	4.80	$2.2 \cdot 10^{-2}$	1.66	8.60	10.44	25.86

Mean value $[Ni^{2+}]^3 \cdot [AsO_4^{3-}]^2 \ldots (3.1 \pm 2.4) \cdot 10^{-26}$

TABLE 7

Solubility and Solubility Product of Aluminum Arsenate at 22°

Solution	pH before shaking	pH of saturated solution	Al^{3+} conc. in g-ions per liter	$p[Al^{3+}]$	pq	$p[AsO_4^{3-}]$	$p[Al^{3+}] \times [AsO_4^{3-}]$
Nitric Acid	3.40	3.65	$2.7 \cdot 10^{-3}$	2.57	10.95	13.52	16.09
	2.20	3.10	$1.2 \cdot 10^{-2}$	1.93	12.10	14.03	15.96
	2.00	3.00	$2.1 \cdot 10^{-2}$	1.68	12.40	14.08	15.76
Sulfuric Acid	3.25	3.50	$5.8 \cdot 10^{-3}$	2.24	11.25	13.49	15.78
	2.25	3.20	$1.1 \cdot 10^{-2}$	1.97	11.85	13.82	15.79
	2.05	3.10	$1.8 \cdot 10^{-2}$	1.73	12.10	13.83	15.56

Mean value $[Al^{3+}] \cdot [AsO_4^{3-}] \ldots (1.6 \pm 0.7) \cdot 10^{-16}$

TABLE 8

Solubility and Solubility Product of Chromium Arsenate at 22°

Solution	pH before shaking	pH of saturated solution	Cr^{3+} conc. in g-ions per liter	$p[Cr^{3+}]$	pq	$p[AsO_4^{3-}]$	$p[Cr^{3+}] \times \times [AsO_4^{3-}]$
Nitric Acid	2.60	2.70	$2.5 \cdot 10^{-4}$	3.60	13.00	16.60	20.20
	2.20	2.30	$9.2 \cdot 10^{-4}$	3.04	13.95	16.99	20.03
	2.00	2.05	$1.7 \cdot 10^{-3}$	2.78	14.60	17.38	20.16
Sulfuric Acid	2.25	2.40	$7.1 \cdot 10^{-4}$	3.15	13.70	16.85	20.00
	2.05	2.15	$1.3 \cdot 10^{-3}$	2.88	14.37	17.25	20.13
	1.80	1.90	$2.9 \cdot 10^{-3}$	2.54	15.00	17.54	20.08

Mean value $[Cr^{3+}] \cdot [AsO_4^{3-}] \ldots (7.8 \pm 1.5) \cdot 10^{-21}$

TABLE 9

Solubility and Solubility Product of Ferric Arsenate at 20°

Solution	pH before shaking	pH of saturated solution	Fe^{3+} conc. in g-ions per liter	$p[Fe^{3+}]$	pq	$p[AsO_4^{3-}]$	$p[Fe^{3+}] \times \times [AsO_4^{3-}]$
Nitric Acid	2.80	2.90	$8.6 \cdot 10^{-5}$	4.07	12.50	16.97	20.64
	2.10	2.20	$8.5 \cdot 10^{-4}$	3.07	14.30	17.37	20.44
	2.00	2.05	$9.4 \cdot 10^{-4}$	3.03	14.60	17.63	20.66
Sulfuric Acid	2.85	2.95	$8.7 \cdot 10^{-5}$	4.06	12.45	16.46	20.57
	2.05	2.15	$1.1 \cdot 10^{-3}$	2.94	14.30	17.24	20.18
	1.90	2.00	$1.9 \cdot 10^{-3}$	2.72	14.75	17.47	20.19
	1.80	1.90	$3.7 \cdot 10^{-3}$	2.43	15.00	17.43	19.86

Mean value $[Fe^{3+}] \cdot [AsO_4^{3-}] \ldots (5.7 \pm 4.2) \cdot 10^{-21}$

TABLE 10

Solubility and Solubility Product of Bismuth Arsenate at 20°

Solution	pH before shaking	pH of saturated solution	Bi^{3+} conc. in g-ions per liter	$p[Bi^{3+}]$	pq	$p[AsO_4^{3-}]$	$p[Bi^{3+}] \times \times [AsO_4^{3-}]$
Nitric Acid	3.25	8.80	$6.6 \cdot 10^{-4}$	3.18	2.70	5.88	9.05
	2.20	6.40	$9.1 \cdot 10^{-3}$	2.04	5.65	7.69	9.73
	2.00	5.70	$3.6 \cdot 10^{-2}$	1.43	6.80	8.23	9.66
Sulfuric Acid	3.20	8.65	$7.2 \cdot 10^{-4}$	3.14	2.85	5.99	9.13
	2.15	6.25	$1.5 \cdot 10^{-2}$	1.82	5.81	7.63	9.47
	1.90	5.60	$5.2 \cdot 10^{-2}$	1.28	7.00	8.28	9.56

Mean value $[Bi^{3+}] \cdot [AsO_4^{3-}] \ldots (4.4 \pm 2.9) \cdot 10^{-10}$

SUMMARY

The solubility products of a series of arsenates have been determined by measuring their solubility in acids at 20°:

$$[Hg^{+}]^{3}\cdot[AsO_4^{3-}] \;\ldots\ldots\; (1.9 \pm 0.6)\cdot 10^{-21}$$
$$[Mn^{2+}]^{3}\cdot[AsO_4^{3-}]^{2} \;\ldots\ldots\; (1.9 \pm 0.7)\cdot 10^{-29}$$
$$[Pb^{2+}]^{3}\cdot[AsO_4^{3-}]^{2} \;\ldots\ldots\; (4.1 \pm 3.6)\cdot 10^{-36}$$
$$[Co^{2+}]^{3}\cdot[AsO_4^{3-}]^{2} \;\ldots\ldots\; (7.6 \pm 4.2)\cdot 10^{-29}$$
$$[Ni^{2+}]^{3}\cdot[AsO_4^{3-}]^{2} \;\ldots\ldots\; (3.1 \pm 2.4)\cdot 10^{-26}$$
$$[Al^{3+}]\cdot[AsO_4^{3-}] \;\ldots\ldots\; (1.6 \pm 0.7)\cdot 10^{-16}$$
$$[Cr^{3+}]\cdot[AsO_4^{3-}] \;\ldots\ldots\; (7.8 \pm 1.5)\cdot 10^{-21}$$
$$[Fe^{3+}]\cdot[AsO_4^{3-}] \;\ldots\ldots\; (5.7 \pm 4.2)\cdot 10^{-21}$$
$$[Bi^{3+}]\cdot[AsO_4^{3-}] \;\ldots\ldots\; (4.4 \pm 2.9)\cdot 10^{-10}$$

Received October 17, 1955

LITERATURE CITED

[1] Whitby, Z. anorg. Chem. 67, 107 (1910).

[2] A. K. Babko, Scientific Proceedings of KDU 4 (1935).

[3] F. G. Zharovsky, Trans. Commission on Anal. Chem. Vol. 3, p. 101 (1951).

[4] I. M. Korenman, J. Gen. Chem. 24, 1910 (1954) (T. p. 1873).*

[5] N. T. Britton, Hydrogen Ions (Gen. Sci. Tech. Press, 1936).

[6] V. F. Hillebrand and G. E. Lendel, Practical Textbook on Inorganic Analysis (Gen. Sci. Tech. Press, 1937).

[7] L. Holborn, Landolt-Börnstein Tabellen (1923), p. 1093.

[8] E. W. Washburn, E. K. Strachan, J. Am. Chem. Soc. 35, 693 (1913).

[9] N. T. Britton, and P. Jackson, J. Chem. Soc. 1934, 1049.

[10] J. Kielland, J. Am. Chem. Soc. 56, 1677 (1937).

[11] W. S. Hughes, J. Chem. Soc. 1928, 502.

[12] A. Skrabal, and A. Zanorka, Z. Elektrochem. 33, 44 (1927).

[13] N. Konorik, and O. Leberl, 80, 668 (1949).

[14] L. M. Batuner and M. E. Pozin, Mathematical Methods in Chemical Technics (State Chem. Press, 1955), p. 384.

---

*T. p. = C. B. Translation pagination.

BLANK
PAGE

EQUILIBRIA IN SOLUTIONS OF PYROPHOSPHATE COMPLEXES

K. B. Yatsimirsky and V. P. Vasilyev

Ivanov Chemico-Technological Institute

Recently, pyrophosphate complexes, in connection with their use in various electro-chemical enterprises and in the chemical analysis of steels have attracted the attention of many investigators. Only during the last 2-3 years have a few articles been published which have been devoted to the study of these complexes.

Despite the large practical significance and theoretical interest attached to these compounds, they have only been studied quantitatively to a comparatively small extent. Only the composition of the complexes has been determined reliably. By means of various physicochemical methods of analysis [1-4], it has been established that the pyrophosphate ion forms complexes of the type $MP_2O_7^{2-}$ and $M(P_2O_7)_2^{6-}$ with simple cations in aqueous solution, where M is a divalent cation (Cu_2^+, Zn^{2+}, Ni^{2+}). Available results on the stability of these compounds are incomplete, and in a number of cases, for copper complexes, results found by different authors differ by a factor of 4-5 times. For the copper complex $CuP_2O_7^{2-}$ Erikson [5], found polarographically that $K_{instability} = 6 \cdot 10^{-14}$, while Watters and Aaron [3], found that $K_{instability} = 2 \cdot 10^{-10}$ by a spectrophotometric method. For the complex ion $Cu(P_2O_7)_2^{6-}$, Stabrovsky [6], by e. m. f. measurements, found $K_{instability} = 3.1 \cdot 10^{-10}$, while Watters and Aaron found $2.7 \cdot 10^{-13}$ by the solubility method. Ukshe and Levin [7], by potentiometric measurements, found $K_{instability}$ for $CuP_2O_7^{2-}$ is $6.3 \cdot 10^{-6}$, while for $Cu(P_2O_7)_2^{6-}$ $K_{instability}$ is $0.5 \cdot 10^{-10}$. We found significant errors in articles [3, 7], connected with calculations of instability constants. These discrepancies, to a large extent, explain the contradictions of the available results on the stability of pyrophosphate complexes of copper. The instability constants of many pyrophosphate complexes have not been determined.

In order to determine the instability constants of the pyrophosphate complexes of copper and nickel, we used the solubility method. We used the normal pyrophosphate salts of these metals $Cu_2P_2O_7$ and $Ni_2P_2O_7$ as the bottom phase. The bottom phase which has in its composition the anion which is the addendum of the complex particle studied (in a given instance, the pyrophosphate ion) is the most suitable, since, in such a case, the possibility of the formation of complexes with differing addenda is excluded. For the preparation of the bottom phase we used chemically pure, and analytically pure preparations of $Cu(NO_3)_2$, $Ni(NO_3)_2$ and $Na_4P_2O_7$. Solutions of cupric nitrate (or nickel nitrate) and sodium pyrophosphate, whose concentrations were known accurately, were mixed in certain fixed proportions. The volumes of the solutions were calculated so that stoichiometric proportions of copper (or nickel) to pyrophosphate were obtained equivalent to $Cu_2P_2O_7$ (or $Ni_2P_2O_7$). The composition of the washed and filtered precipitate after drying at 110° corresponded to the formula $Cu_2P_2O_7 \cdot 1^1/_3\ H_2O$ or $Ni_2P_2O_7 \cdot 5^1/_2\ H_2O$ (by chemical analysis.

Solubility determinations were carried out in 100 ml narrow necked flasks. An aliquot of the air dried bottom phase (of known moisture content) was placed in a flask which contained an accurately measured volume of a standard solution of sodium pyrophosphate (50-70 ml). The flasks were closed with rubber bungs and placed in a water thermostat, in which the temperature was kept at 25 ± 0.01°. The water thermostat in turn was kept inside an air thermostat with a temperature of 25 ± 0.1°. The flasks placed inside the thermostat cradle were agitated by means of a special crankshaft mechanism, which made 80-90 vibrations a minute. Preliminary experiments indicated that equilibrium is reached after 3-4 hours in the case of copper pyrophosphate solutions; solutions of nickel pyrophosphate take 80-100 hours to reach equilibrium. When equilibrium had been reached, the solution was filtered through a sintered glass filter. Filtration was carried out in the air thermostat under a slight vacuum from a water pump, and took 4-5 minutes after standing in the air thermostat for 4-5 hours. Copper or nickel, respectively were determined in the filtrate; sometimes, phosphorus as well. The bottom phase was analyzed at extreme points of the studied concentration range of the pyrophosphate. No changes in the composition of the bottom phase were detected.

TABLE 1

Solubility of $Cu_2P_2O_7$ in $Na_4P_2O_7$ Solution

Original concentration of $Na_4P_2O_7$ in moles/liter	Equilibrium concentration of $P_2O_7^{4-}$ in moles/liter	Solubility of $Cu_2P_2O_7$ in moles/liter		Difference $S_{calc} - S_{exptl}$
		calculated by Equation (11)	determined experimentally	
0.0262	0.0055	0.0110	0.0110	0.0000
0.0276	0.0057	0.0112	0.0114	−0.0002
0.0409	0.0079	0.0162	0.0159	0.0003
0.0502	0.0092	0.0192	0.0190	0.0002
0.0527	0.0095	0.0200	0.0199	0.0001
0.0640	0.0111	0.0233	0.0236	−0.0003
0.0715	0.0120	0.0263	0.0261	0.0002
0.0874	0.0139	0.0314	0.0313	0.0001
0.1015	0.0155	0.0358	0.0359	−0.0001

TABLE 2

Solubility of $Ni_2P_2O_7$ in $Na_4P_2O_7$ Solutions

Original concentration of $Na_4P_2O_7$ in moles/liter	Equilibrium concentration of $P_2O_7^{4-}$ in moles/liter	Solubility of $Ni_2P_2O_7$ in moles/liter		Difference $S_{calc} - S_{exptl}$
		calculated by Equation (12)	determined experimentally	
0.0338	0.0093	0.0149	0.0159	−0.0010
0.0356	0.0100	0.0156	0.0163	−0.0007
0.0444	0.0128	0.0187	0.0191	−0.0004
0.0502	0.0143	0.0204	0.0208	−0.0004
0.0687	0.0193	0.0258	0.0263	−0.0005
0.0841	0.0236	0.0308	0.0306	0.0002
0.1057	0.0293	0.0378	0.0370	0.0008
0.1226	0.0319	0.0406	0.0428	−0.0022

Determination of copper in solution was carried out iodometrically by Bruns' method [9] (iodide and thiocyanate solutions were used).

In those cases where it was necessary to determine phosphorus, copper was removed from solution electrolytically; the solution was then heated with nitric acid to convert pyrophosphate to orthophosphate [8]; precipitation was carried out with a magnesia mixture. The precipitate was calcined to give magnesium pyrophosphate. Nickel was determined gravimetrically as the dimethylglyoximate; phosphorus was determined in the filtrate after removal of nickel by the method indicated above. Results of solubility determinations are given in Tables 1 and 2. Solubility values are given on the basis of determinations of the contents of the corresponding cations in solution.

In addition to determinations of solubility in sodium pyrophosphate solutions, the solubility of the same pyrophosphates was also studied in water containing potassium nitrate. The solubility of copper pyrophosphate in potassium nitrate solutions with molarity ranging from 0.5 to 1.0 amounted to $(6.5 \pm 0.3) \times 10^{-5}$ moles/liter; the corresponding value for nickel pyrophosphate was $(3.4 \pm 0.2) \times 10^{-4}$ moles/liter. Copper was determined colorimetrically as the rubeanate [10], while nickel was determined in the form of the compound with dimethylglyoxime oxidized by bromine [11]. Colorimetric determinations were carried out with the usual colorimeter loadings.

DISCUSSION OF RESULTS

In agreement with published results on the composition of the pyrophosphate complexes of copper [1-3], and nickel [2, 4], the increase in solubility of the bottom phase on addition of sodium pyrophosphate can be explained by the occurrence of the following processes:

$$M_2P_2O_7\ \text{solid state} + P_2O_7^{4-} \rightleftharpoons 2MP_2O_7^{2-}, \tag{I}$$

$$M_2P_2O_7\ \text{solid state} + 3P_2O_7^{4-} \rightleftharpoons 2M(P_2O_7)_2^{6-} \tag{II}$$

(M is either Cu or Ni).

In addition, the bottom phase dissolves in water independently of complex formation processes

$$M_2P_2O_7\,\text{solid state} \rightleftharpoons M_2P_2O_7\,\text{solution} \tag{III}$$

$$M_2P_2O_7 \rightleftharpoons M^{2+} + MP_2O_7^{2-} \rightleftharpoons 2M^{2+} + P_2O_7^{4-} \tag{IV}$$

Tests showed that the value of the solubility of copper and nickel pyrophosphates respectively, is much less in water than in sodium pyrophosphate solutions. The solubility in water, which is not connected with complex formation, is low, but it is to be expected that it will be even lower in sodium pyrophosphate solutions, since the similar ion (the pyrophosphate ion) effect will decrease solubility according to Scheme (IV). Consequently, one can assume that all the copper or nickel in solution, is complexed as $MP_2O_7^{2-}$ and $M(P_2O_7)_2^{6-}$. Thus the solubility of the bottom phase in sodium pyrophosphate solutions can be expressed by the relation:

$$S = {}^1\!/_2 c_{MP_2O_7^{2-}} + {}^1\!/_2 c_{M(P_2O_7)_2^{6-}}. \tag{1}$$

The concentrations of the complexes $c_{MP_2O_7^{2-}}$ and $c_{M(P_2O_7)_2^{6-}}$ can be expressed by the equilibrium concentration of the pyrophosphate, by using the expression for the instability constants of the complexes, and the expression for the solubility product of the bottom phase. In such a case, Expression (1) assumes the form

$$S = \alpha c^{1/2}_{P_2O_7^{4-}} + \beta c^{3/2}_{P_2O_7^{4-}}, \tag{2}$$

$$\alpha = \frac{L_p^{1/2}}{2k_{MP_2O_7^{2-}}}, \tag{2a}$$

$$\beta = \frac{L_p^{1/2}}{2k_{M(P_2O_7)_2^{6-}}}, \tag{2b}$$

where L_p is the solubility product of the bottom phase $M_2P_2O_7$ and $k_{MP_2O_7^{2-}}$ and $k_{M(P_2O_7)_2^{6-}}$ the instability constants, corresponding to the complex ion $MP_2O_7^{2-}$ and $M(P_2O_7)_2^{6-}$ (total).

The constants in Equation (2) can be found readily, as long as the equilibrium concentrations of the pyrophosphate are known (solubility is determined experimentally). We used the following procedure for calculating the equilibrium concentration of pyrophosphate.

In a physical sense, the equilibrium concentration of pyrophosphate is determined by the difference

$$c_{P_2O_7^{4-}} = c_{\text{total}} - c_{\text{complexed}} \tag{3}$$

where c_{total} is the total pyrophosphate concentration in solution

$$c_{\text{total}} = c_{\text{original}} + S, \tag{3a}$$

where c_{original} is the original sodium pyrophosphate concentration; S, the solubility of $M_2P_2O_7$ in a solution of sodium pyrophosphate with a concentration of c_{original}; $c_{\text{complexed}}$, the concentration of pyrophosphate complexed as $MP_2O_7^{2-}$ and $M(P_2O_7)_2^{6-}$:

$$c_{\text{complexed}} = c_{MP_2O_7^{2-}} + 2c_{M(P_2O_7)_2^{6-}}. \tag{3b}$$

In calculating the equilibrium concentration of the addendum one should take into account the decrease in pyrophosphate concentration as a result of hydrolysis. Nevertheless, the magnitude of this effect is considerably less than the equilibrium concentration; accordingly we disregarded it.

Taking into account Expressions (3a) and (3b), Expression (3) transforms into

$$c_{P_2O_7^{4-}} = c_{\text{original}} + S - c_{MP_2O_7^{2-}} - 2c_{M(P_2O_7)_2^{6-}}. \tag{4}$$

Taking into account the analytical relationship between solubility and equilibrium concentration of the addendum, and using the expression for the intermediate stability constant of the complex $M(P_2O_7)_2^{6-}$ (designated henceforth by $\varkappa$), we simplified Expression (4), and got:

$$c_{P_2O_7^{4-}} = c_{\text{original}} - \frac{1 + 3\varkappa c_{P_2O_7^{4-}}}{1 + \varkappa c_{P_2O_7^{4-}}} S. \tag{5}$$

In Equation (5), the multiplier in front of S may change from unity, in cases where only one complex $MP_2O_7^{2-}$ exists in solution, to three when only the second complex $M(P_2O_7)_2^{6-}$ is found in solution.

Equation (2) shows that with increasing equilibrium concentration of pyrophosphate, solubility increases; consequently, the original pyrophosphate concentration and the equilibrium change in line with each other. To a first approximation therefore, one can assume a proportionality

$$\varkappa c_{P_2O_7^{4-}} = \gamma c_{\text{original}}, \tag{6}$$

where γ is an empirical constant. Equation (5) then assumes the form

$$c_{P_2O_7^{4-}} = c_{\text{original}} - \frac{1 + 3\gamma c_{\text{original}}}{1 + \gamma c_{\text{original}}} S. \tag{7}$$

At some point on the solubility curve, the multiplier which precedes S is equal to two. Let us assume that this point lies mid way along the solubility curve. One could assume that this point lies either at the beginning or the end of the solubility curve – such an assumption is arbitrary to a considerable extent. We are free from this in the second approximation since then the equilibrium concentrations of the addendum will be evaluated. When the multiplier which precedes S in Equation (7) is equal to 2

$$\frac{1 + 3\gamma c_{\text{original}}}{1 + \gamma c_{\text{original}}} = 2 \tag{7a}$$

in the middle of the solubility curve, then, having solved Equation (7a) with respect to γ, it is possible, using Equation (7), to calculate the equilibrium concentrations of the pyrophosphate to a first approximation over all the concentration range tested.

For accurate calculation of equilibrium concentrations, it is essential to know $\varkappa$ – the intermediate instability constant of the complex $M(P_2O_7)_2^{6-}$, since this would allow one to solve Equation (5) with respect to $c_{P_2O_7^{4-}}$ without making any assumptions.

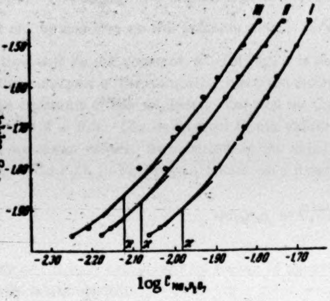


Fig. 1. Calculation of the equilibrium concentration of $P_2O_7^{4-}$ during solution of $Cu_2P_2O_7$ in $Na_4P_2O_7$.

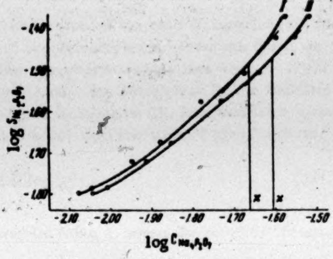


Fig. 2. Calculation of the equilibrium concentration of $P_2O_7^{4-}$ during solution of NiP_2O_7 in $Na_4P_2O_7$.

One could evaluate $\varkappa$ by means of a logarithmic graph using the values of the equilibrium concentrations of the addendum obtained to a first approximation.

It is necessary to transform the solubility Equation (2) a little, and take logarithms

$$\log S = \log \alpha + {}^1/_2 \log c_{P_2O_7^{4-}} + \log(1 + \varkappa c_{P_2O_7^{4-}}), \qquad (8)$$

and then to differentiate with respect to logarithm $c_{P_2O_7^{4-}}$

$$\frac{\partial \log S}{\partial \log c_{P_2O_7^{4-}}} = {}^1/_2 + \frac{\varkappa c_{P_2O_7^{4-}}}{1 + \varkappa c_{P_2O_7^{4-}}}. \qquad (9)$$

At the point where $\varkappa c_{P_2O_7^{4-}} = 1$, the product assumes the value

$$\frac{\partial \log S}{\partial \log c_{P_2O_7^{4-}}} = 1. \qquad (9a)$$

From graph log S − log $c_{P_2O_7^{4-}}$ it is possible to find $\varkappa$ as the abscissa of the point of intersection of the tangent drawn at 45° to the curve obtained.

The value of $\varkappa$ found in this way can be used for a more accurate solution of Equation (5) relative to $c_{P_2O_7^{4-}}$. Another graph of logarithm S − logarithm $c_{P_2O_7^{4-}}$ is then drawn on the basis of the new values and new values of $\varkappa$ again found graphically. By repeating the calculations one gets results which agree with each other in two successive approximations. Successive approximations during calculation of equilibrium concentration of pyrophosphate in the case of the solution of copper pyrophosphate are illustrated on Fig. 1, while the solution of nickel pyrophosphate is shown in Fig. 2.

The equilibrium concentrations of pyrophosphate determined experimentally during formation of copper complexes are given in Table 1, while those found during formation of nickel complexes are given in Table 2.

Equation (2) can be transformed into that for a straight line by introducing a new variable*. For this purpose let us divide (2) by $c_{P_2O_7^{4-}}^{1/2}$.

$$\frac{S}{c_{P_2O_7^{4-}}^{1/2}} = \alpha + \beta c_{P_2O_7^{4-}}. \qquad (10)$$

---

*A similar method was suggested by I. Lendel [12], for treating results obtained by a potentiometric method.

If $S/c_{P_2O_7^{4-}}^{1/2}$ and $c_{P_2O_7^{4-}}$ are regarded as variables, Equation (10) will become the equation for a straight line. The segment cut by this line on the ordinate axis ($S/c_{P_2O_7^{4-}}^{1/2}$) will be equal to α numerically, while the slope of the line will be the constant β. On Fig. 3 is shown a curve constructed on the basis of Equation (10) for calculating the constants of the solubility equation during formation of copper complexes. From this graph we found that the constants of the solubility equation for $Cu_2P_2O_7$ in sodium pyrophosphate solutions were $\alpha = 0.072 \pm$ $\pm\ 0.004$; $\beta = 14.2 \pm 0.5$. The deviations in the values of α and β indicated, were determined by the boundary method, and are mean values. By substituting the values of α and β found in Equation (2), it is possible to express the solubility of $Cu_2P_2O_7$ in $Na_4P_2O_7$ solutions as a function of the equilibrium concentration of pyrophosphate.

$$S_{Cu_2P_2O_7} = 0{,}072 c_{P_2O_7^{4-}}^{1/2} + 14.2 c_{P_2O_7^{4-}}^{3/2}. \tag{11}$$

The solubility of $Cu_2P_2O_7$ calculated by means of Equation (11) is given in Table 1, where the solubility determined experimentally is also given.

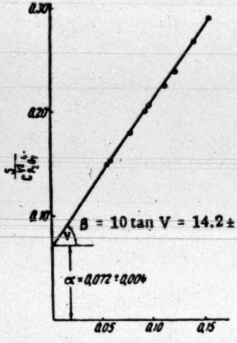


Fig. 3. Determination of the constants α and β of Equation (2) during solution of $Cu_2P_2O_7$.

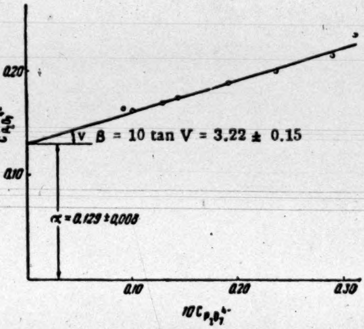


Fig. 4. Determination of the constants α and β of Equation (2) during solution of NiP_2O_7.

As is evident from the results given in Table 1, the deviation between the calculated values of the solubility, and those found experimentally, is not very great and does not exceed 2%.

Calculation of the constants for the solubility equation for nickel complexes was carried out on the basis of the graph shown on Fig. 4.

The constants of the solubility equation of $Ni_2P_2O_7$ in sodium pyrophosphate solutions were found to be $\alpha = 0.120 \pm 0.008$; $\beta = 3.22 \pm 0.15$ The relation between the solubility of $Ni_2P_2O_7$ and the equilibrium concentration of pyrophosphate will accordingly be expressed by:

$$S_{NiP_2O_7} = 0{,}12 c_{P_2O_7^{4-}}^{1/2} + 3{,}22 c_{P_2O_7^{4-}}^{3/2}. \tag{12}$$

A comparison of the solubility of $Ni_2P_2O_7$ in sodium pyrophosphate solutions, calculated from Equation (12), with those found experimentally is given in Table 2. Deviation between experimental and calculated results does not exceed 6.3%.

The constants found for the solubility Equations (11) and (12), are connected via Relations (2a) and (2b) with the instability constants of the complexes and the solubility product of the bottom phase. We calculated the solubility products from the solubility of the bottom phase in water (with addition of potassium nitrate). Copper and nickel pyrophosphates do not dissociate completely on dissolving in water. Judging by published results, the complex ion $MP_2O_7^{2-}$ is a fairly stable particle, and its dissociation in solution will be suppressed by the common ion M^{2+}. We shall therefore regard the pyrophosphates under discussion, $M_2P_2O_7$, as salts of type MX, where X is the doubly charged anion $MP_2O_7^{2-}$. Compounds of this type in solution, as published results indicate, either dissociate completely or form unstable complexes. This means that the position of the equilibrium during the process

$$M_2P_2O_7 \rightleftarrows M^{2+} + MP_2O_7^{2-} \qquad \text{(V)}$$

is shifted practically completely to the right hand side. The concentration product of ions M^{2+} and $MP_2O_7^{2-}$ can be regarded as a step-wise or successive solubility product, by analogy with the step-wise dissociation constants of polybasis acids and the successive instability constants of the complexes. Taking into account the considerations outlined above on the displacement of the Equilibrium (V), one can, in the given instance, find the step-wise solubility product directly from the value for the solubility of the bottom phase in water (S_0)

$$L_{Pc} = c_{M^{2+}} \cdot c_{MP_2O_7^{2-}} = S_0^2. \qquad (13)$$

The step-wise solubility product is related to total Lp by the simple relation:

$$L_P = L_{P_c} \cdot K_{MP_2O_7^{2-}}. \qquad (14)$$

The constant α in Expression (2a) can be expressed by the step-wise solubility product

$$\alpha = \frac{L_{Pc}^{1/2}}{2K_{MP_2O_7^{2-}}^{1/2}}.$$

From Relation (15) it is possible to find the instability constants of complexes of the type $MP_2O_7^{2-}$.

Having determined $K_{MP_2O_7^{2-}}$, the total solubility product is calculated from Equation (14), and then from Relation (2b) the instability constants of complex ions of type $M(P_2O_7)_2^{6-}$ found. Constants calculated by this method are given in Table 3. The accuracy of the values obtained for the instability constants depends, as is evident from Relations (2a), (2b), and (15), on the accuracy of determination of L_{PC} and the coefficients α and β of the solubility equations. Deviations in the values given in Table 3, were calculated by differentiating Equations (13), (14), (15), and (2b) and substituting in the expressions obtained the corresponding final increments.

TABLE 3

Solubility Products of Copper and Nickel Pyrophosphates, and the Total Instability Constants of the Pyrophosphate Complexes

Element	Solubility product		Instability constants	
	stepwise $[M^{2+}][MP_2O_7^{2-}]$	total $[M^{2+}][P_2O_7^{4-}]$	$MP_2O_7^{2-}$	$M(P_2O_7)_2^{6-}$
Cu	$(4.2 \pm 0.4)\cdot 10^{-9}$	$(8.4 \pm 2.5)\cdot 10^{-16}$	$(2.0 \pm 0.4)\cdot 10^{-7}$	$(1.0 \pm 0.2)\cdot 10^{-9}$
Ni	$(1.1 \pm 0.1)\cdot 10^{-7}$	$(1.7 \pm 0.4)\cdot 10^{-13}$	$(1.5 \pm 0.5)\cdot 10^{-6}$	$(6.5 \pm 2.9)\cdot 10^{-8}$

The value which we found for the instability constant of the complex $Cu(P_2O_7)_2^{6-}$ is close to that found by Stabrovsky [6] – $3.1 \cdot 10^{-10}$. If one corrects the results of the American authors [3], by taking into account the instability constants of the copper oxalate complex, found by Yatsimirsky and Zolotarev [13], then, in this case, the instability constant of $Cu(P_2O_7)_2^{6-}$, approximates to the value which we found (it becomes $2.2 \cdot 10^{-10}$). The instability constants of the pyrophosphate complexes of nickel were determined first.

SUMMARY

1. The solubility of copper and nickel pyrophosphates respectively has been determined in sodium pyrophosphate solutions of various concentrations, and in water to which potassium nitrate has been added.

2. The instability constants of the complex ions $CuP_2O_7^{2-}$, $Cu(P_2O_7)_2^{6-}$, $NiP_2O_7^{2-}$, $Ni(P_2O_7)_2^{6-}$ have been calculated, as well as the solubility products of the sparingly soluble salts $Cu_2P_2O_7$ and $Ni_2P_2O_7$.

Received January 14, 1955.

LITERATURE CITED

[1] B. C. Haldar, Science and Culture 14, 340 (1949); cited in C. A. 43, 6103 (1949).

[2] L. Rogers and C. Reynolds, J. Am. Chem. Soc. 71, 2081 (1949).

[3] G. Watters and A. Aaron, J. Am. Chem. Soc. 75, 611 (1953).

[4] B. C. Haldar, Nature 166, 744 (1950).

[5] E. Erikson, Kgl. Lantbruks. Högskoll. Ann. 16, 39 (1949); cited in C. A. 44, 3392 (1950).

[6] A. I. Stabrovsky, J. Phys. Chem. 26, 949 (1952).

[7] E. A. Ukshe and A. I. Levin, J. Gen. Chem. 24, 775 (1954) (T. p. 781).*

[8] I. M. Kolthoff and V. A. Stenger, Volumetric Analysis (State Chem. Press, Moscow-Leningrad, 1952), Vol. II.

[9] V. F. Hillebrand and G. E. Lendel, Practical Textbook on Inorganic Analysis (Gen. Sci. Tech. Press, Moscow, 1935).

[10] W. Miller, G. Geld and M. Quantinetz, Anal. Chem. 22, 1572 (1950).

[11] A. K. Babko and A. G. Pilipenko, Colorimetric Analysis (State Chem. Press, Moscow-Leningrad, 1951).

[12] J. Leden, Z. physik. Chem. 188, 160 (1941).

[13] K. B. Yatsimirsky and E. K. Zolotarev, J. Phys. Chem. 28, 1292 (1954).

---

*T. p. = C. B. Translation pagination.

THE POLAROGRAPHIC CATALYTIC CURRENT OF MOLYBDENUM AND ITS USE FOR DETERMINING MICRO-GRAM AMOUNTS OF MOLYBDENUM

S. I. Sinyakova and M. I. Glinkina

The Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow

Small amounts of molybdenum are usually determined colorimetrically as the thiocyanate [1]. It is also possible to use the catalytic properties of molybdenum for analytical purposes as Sinyakova [2] proposed for determination of copper. Actually, Yatsimirsky and Afanasyeva [3] have shown that molybdenum even at concentrations of 10^{-7} - 10^{-6} M catalyzes the oxidation of iodide by hydrogen peroxide, so that by measuring the rate of this reaction, it is possible to determine these very small amounts of molybdenum. Variants of the polarographic method have also been proposed for determining molybdenum [4].

Of the greatest interest is the polarographic determination of molydbenum in the presence of Trilon B, whereby it is possible to determine molybdenum in the presence of tungsten and other elements (Pb, Cd, Zn) in solution [5]. All the same, for determining 10^{-4} - 10^{-5}% of Mo, normal polarographic and colorimetric methods are of low sensitivity. Tungsten and other elements interfere with the use of the catalytic method for this purpose.

In recent years, polarographic catalytic currents have been studied; they have been used for determining very small amounts of certain elements.

Kolthoff and Parry [6], have studied the catalytic effect of hydrogen peroxide during reduction of trivalent iron on a dropping mercury cathode; they explain the increase in the limiting current of trivalent iron by the appearance of an additional current limited by the velocity of the following reaction on the electrode surface

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \qquad (1)$$

with subsequent reduction of regenerated Fe^{3+}. The same authors [7], found similar currents limited by the reaction kinetics in the case of molybdate, tungstate, and vanadate in the presence of hydrogen peroxide. In the authors' opinions, the mechanism of the processes, in particular, for the molybdate ion, reduces to the fact that the molybdate reacts in acid solutions with hydrogen peroxide to form the peroxide compound:

$$MoO_4^{2-} + H_2O_2 \rightarrow MoO_5^{2-} + H_2O, \qquad (2)$$

which is reduced on the dropping mercury cathode to form the molybdate ion

$$MoO_5^{2-} + 2H^+ + 2e \rightarrow MoO_4^{2-} + H_2O. \qquad (3)$$

In this way uninterrupted regeneration of molybdate ions takes place. The magnitude of the catalytic current of molybdenum is determined by the reaction rate [2], and since it is large, then even when molybdate ion concentrations are very low, measurable currents are obtained.

Blazek and Koryta [8], detected a catalytic wave during reduction of the oxalate complex of quadrivalent titanium in the presence of hydroxylamine. The theory of catalytic currents has been developed by Meiman, Koutecky et al [9].

Molybdenum gives catalytic waves in sulfuric acid solutions containing the nitrate ion [10], and also in perchloric acid solutions. The latter has been used for determining molybdenum, on the basis of its catalytic wave, in iron and steels [11], while its sodium salt in sulfuric acid solutions has been used for determining molybdenum in plants [12].

In the work described in the present article, the catalytic current of molybdenum in perchloric acid and sodium perchlorate solutions has been studied; in addition, the possibility of using the catalytic current for determining micro-gram amounts of molybdenum, particularly in ores, has also been clarified.

EXPERIMENTAL

Measurements were carried out on a Heyrovsky type recording polarograph using a mirror galvanometer with a sensitivity of $3.33 \cdot 10^{-9}$ A/mm/m. A 3 ml electrolytic cell was used. The capillary characteristics were as follows: $m = 1.98$ mg/sec^{-1}; $t = 4.2$ sec; $m^{2/3}t^{1/6} = 2.003$ mg$^{2/3} \cdot$sec$^{-1/2}$. The anode was a saturated calomel electrode connected to the electrolytic cell via an agar-agar bridge prepared from a semi-saturated potassium chloride solution. All half-wave potentials are referred to the saturated calomel electrode.

Molybdate solutions were prepared from MoO_3, obtained by calcining ammonium molybdate at 500°. An aliquot of MoO_3 was dissolved in a small amount of ammonia solution; excess of the latter was removed by boiling and the solution made up to the requisite volume. The solutions had a pH of 6-7. The molybdenum in the solutions was determined gravimetrically as lead molybdate. α-Benzoinoxime was prepared by dissolving 2 g reagent in 100 ml ethyl alcohol.

1. Behavior of the Molybdate Ion in 0.1 M H_2SO_4 – 0.2 M Na_2SO_4

The molybdate ion is reduced in solutions of 0.1 M H_2SO_4–0.2 M Na_2SO_4, to give 3 waves; the half-wave potential of Mo depends to some extent on molybdenum concentration. Thus $E_{1/2}$ of the second molybdenum wave is −0.32 and −0.28 V respectively at concentrations of 0.52 and 0.052 millimole/liter. At low molybdenum concentrations, there is not a sufficiently clear cut line of demarcation between the second and third waves, and the limiting current of the second wave fuses into the beginning of the reduction current of the third wave (Fig. 1); this interferes with exact determination of the limiting current during the second stage of molybdenum reduction.

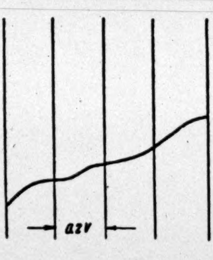


Fig. 1. Diffusion wave of Mo in a supporting electrolyte of 0.1 M H_2SO_4 – 0.2 M Na_2SO_4.

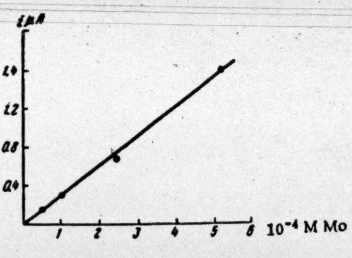


Fig. 2. Relation between the values of the diffusion current and Mo concentration in a supporting electrolyte of 0.1 M H_2SO_4 – 0.2 M Na_2SO_4.

There is a linear relation between the value of the limiting current of the second wave and molybdenum concentration in solution (Fig. 2). The diffusion current constant of the second stage of molybdenum reduction, in 0.1 M H_2SO_4–0.2 M Na_2SO_4 – $K = \frac{i_d}{Cm^{2/3} \cdot t^{1/6}}$ = 1.40 micro-amps/mm/liter, which indicates that the electrode reduction of Mo^V is a one-electron process and leads to the mechanism

$$Mo^{V} + e \rightarrow Mo^{IV}. \qquad (4)$$

The diffusion coefficient of Mo^V calculated by the Ilkovich equation is $D = 0.54 \cdot 10^{-5}$ $cm^2 \cdot sec^{-1}$.

Since the absolute values of the molybdenum current in a solution of 0.1 M H_2SO_4 − 0.2 M Na_2SO_4 are small, then, for analytical purposes, we studied the catalytic currents of molybdenum in solutions of perchloric acid and its sodium salt.

2. The Catalytic Wave of Molybdenum in 1M $HClO_4$ − 0.75 M H_2SO_4 Solution

In 1 M $HClO_4$−0.75 M H_2SO_4 solution a large wave is obtained for molybdate, which has a half-wave voltage of $E_{1/2} = -0.32$ V(Fig. 3, Curve 2), and which depends on molybdenum concentration. The position of this wave on the potential axis corresponds to the second stage of reduction of the molybdate ion in 0.0 M H_2SO_4 − 0.2 M Na_2SO_4, i. e. reduction of Mo^V. The size of this current indicates its catalytic nature, and, consequently, is determined by regeneration of Mo^V as a consequency of the oxidation of the product of the electrode reaction, Mo^{IV} or Mo^{III}, by means of $HClO_4$. Below it will be shown what reduction product of Mo^V is responsible for the development of the catalytic wave. Since most of the tests were carried out in solutions of 1 M $NaClO_4$ − 0.75 M H_2SO_4 then in the case of the electrolyte 1 M $HClO_4$ − 0.75 M H_2SO_4, we have confined ourselves to results in Table 1 which characterize the relation between the value of the catalytic current of molybdenum and its concentration.

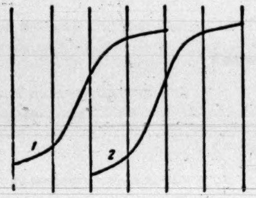


Fig. 3. Curve 1) $2.6 \cdot 10^{-4}$ M molybdate in a solution of 1 M $NaClO_4$ − 0.75 M H_2SO_4. S = 1/100; Curve 2) $2.6 \cdot 10^{-4}$ molybdate in a solution of 1 M $HClO_4$ − 0.75 M H_2SO_4. S = 1/100.

As can be seen from Table 1, there is no linear relation between the value of the catalytic current of molybdenum and its concentration in solution. With decreasing molybdenum concentration, the "apparent" diffusion current constant $K = i_k/C$, increases. Nevertheless, within very narrow concentration limits of molybdenum, a linear relation between molybdenum concentration and the value of the catalytic current is observed, as follows from the last three results of Table 1. By constructing a calibration curve it is possible to determine molybdenum by means of its catalytic wave in 1 M $HClO_4$ − 0.75 M H_2SO_4 solution.

3. The Catalytic Wave of Molybdenum in 1 M $NaClO_4$ − 0.75 M H_2SO_4 Solution

We studied the catalytic wave of molybdenum in a solution of 1 M $NaClO_4$ − 0.75 M H_2SO_4 in more detail. The half-wave potential of the molybdenum catalytic wave in this solution is −0.32 V, and depends on molybdenum concentration (Fig. 3, Curve 1).

In order to establish the nature of the current obtained we studied the relation between size of the limiting current and height of the mercury column. This relationship is illustrated on Fig. 4 and in Table 2 for two molybdenum concentrations of $5.2 \cdot 10^{-5}$ and $2.1 \cdot 10^{-5}$ M/liter.

TABLE 1

Relation Between the Molybdenum Catalytic Current and its Concentration in 1 M $HClO_4$ − 0.75 M H_2SO_4

Mo in γ/ml	Mo M·10^{-4}	i_k in micro-amps	Mean i_k in micro-amps	$K = i_k/C$
50	5.2	18.48; 18.81; 18.98; 18.65	18.73	36
25	2.6	10.34; 10.84; 10.65	10.61	41
10	1.04	5.99; 5.65; 5.99; 5.99	5.90	57
5	0.52	3.20; 3.00; 3.20; 3.20	3.15	61
2	0.21	1.46; 1.37; 1.27	1.37	65
1	0.105	0.666; 0.699; 0.732	0.70	67

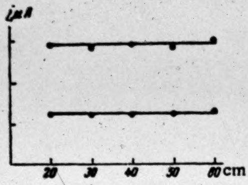


Fig. 4. Relation between the catalytic current of molybdenum and height of the mercury column, for two different Mo concentrations.

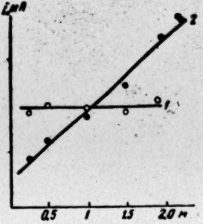


Fig. 5. Curve 1) the relation between the value of the Mo catalytic current and sulfuric acid concentration; Curve 2) relation between current and $NaClO_4$ concentration.

TABLE 2

Relation Between Limiting Current of Molybdenum and the Height of the Mercury Column at Varying Concentrations

Concentration Mo $5.2 \cdot 10^{-5}$ M/liter					
Height of mercury column, cm	20	30	40	50	60
i_k in micro-amps	2.89	2.73	2.99	2.92	3.06
Concentration Mo $2.10 \cdot 10^{-5}$ M/liter					
Height of mercury column, cm	20	30	40	50	60
i_k in micro-amps	1.232	1.232	1.248	1.225	1.248

As is evident from Fig. 4, the value of the limiting current of molybdenum is independent of the mercury column pressure; this indicates that the current obtained is determined not only by diffusion, but also by the rate of the chemical reaction.

Next, the effect of the concentration of both the components of the supporting electrolyte was studied. With this aim in view, polarograms were taken of $1.04 \cdot 10^{-4}$ M solutions of molybdenum in a supporting electrolyte of 1 M $NaClO_4$ containing varying amounts of H_2SO_4, and also in a supporting electrolyte of 0.75 M H_2SO_4 containing varying amounts of $NaClO_4$, or $HClO_4$ respectively (Figs. 5, 6).

As can be seen from Figs. 5 and 6, sulfuric acid concentration has no effect on the value of the catalytic current of molybdenum; the sodium perchlorate or $HClO_4$ concentrations respectively on the other hand have a considerable effect. The catalytic current increases with increasing concentration of $HClO_4$ up to 7 M, then, after passing through a maximum, it falls to zero at a concentration of 10 M $HClO_4$. It follows from this that the catalytic current of molybdenum arises as a result of a chemical reaction between the product of the electrode reduction of Mo^V and perchloric acid.

In order to find out what product of the electrode reduction of Mo^V is oxidized by perchloric acid (Mo^{IV} or Mo^{III}), we took polarograms of solutions of Mo^{IV} and Mo^{III} in the same supporting electrolyte, i. e. in a solution of 1 M $NaClO_4$ – 0.75 M H_2SO_4.

Mo^{IV} solutions were prepared by reducing a solution of ammonium molybdate by means of $FeSO_4$ with slight heating for ~5 minutes; solutions of Mo^{III} were prepared by passing ammonium molybdate solution containing 0.75 M H_2SO_4 through a reducing apparatus containing cadmium obtained electrolytically. In the last instance, the solution from the reducing apparatus was collected directly in the electrolytic cell, hydrogen being passed through the solution continuously. Sodium perchlorate was added to the solution in the electrolytic cell till its concentration was 1 M, when polarograms were taken (Fig. 7). Curve 1 was obtained with a solution of Mo^{VI}; Curve 2 with Mo^{IV} solution, while Curve 3 was obtained with a Mo^{III} solution.

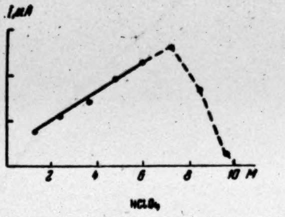


Fig. 6. Relation between the size of the catalytic current of Mo and $HClO_4$ concentration.

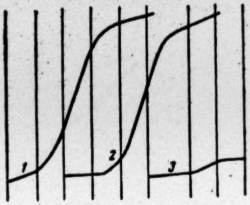


Fig. 7. Curve 1) $5.2 \cdot 10^{-4}$ M molybdate in a solution of 1 M $NaClO_4$ – 0.75 M H_2SO_4, S = 1/100; Curve 2) the same amount of molybdate reduced by $FeSO_4$ to Mo^{IV}, in the same supporting electrolyte, S = 1/100; Curve 3) the same amount of molybdate reduced in a reducing apparatus to Mo^{III}, in the same supporting electrolyte, S = 1/100.

At concentrations of 50 γ/ml of Mo, the limiting current in solutions of Mo^{VI}, Mo^{IV}, and Mo^{III} was 18.40, 17.82*, and 1.48 micro-amps.

In Mo^{IV} solutions the value of the catalytic current is the same as that obtained in Mo^{VI} solutions, while in Mo^{III} solutions the current is very small, presumably, as the result of partial oxidation of Mo^{III} to Mo^{IV}. Consequently, the catalytic current of molybdenum is the result of oxidation of Mo^{IV}, obtained during electrode reduction of Mo^{V}, and the mechanism of the processes can be represented by the following equations:

$$Mo^{V} + e \rightarrow Mo^{IV}, \qquad (6)$$

$$8Mo^{IV} + ClO_4^- + 8H^+ \rightarrow 8Mo^{V} + Cl^- + 4H_2O.$$

The Mo^{V} formed is again reduced on the dropping mercury electrode; this explains the increase in the limiting current. Formation of Cl' according to Equation (6) was confirmed by us by means of a qualitative reaction with silver nitrate after a long electrolysis at −0.8 V.

In order to find out whether or not a linear relationship is maintained between the size of the catalytic current and the molybdenum concentration in solution, polarograms were taken of molybdenum solutions using 1M $NaClO_4$ – 0.75 M H_2SO_4 as supporting electrolyte, the concentration of molybdenum being varied. The results obtained are given in Table 3 and on Fig. 8.

As is evident from Table 4 and Fig. 8, no linear relation is observed between the value of the catalytic current of molybdenum and its concentration in solution; this is characteristic of catalytic currents in general. All the same, within narrow concentration limits, this relationship holds (Fig. 9).

With decreasing molybdenum concentration, the currents are relatively enhanced; nevertheless, for analytical purposes one can use a calibration curve (Fig. 8) by means of which it is possible to determine very small amounts of molybdenum with an accuracy of up to 5-10%. Molybdenum can be determined by means of the catalytic wave at concentrations down to $1 \cdot 10^{-6}$ M/liter, i. e. 0.1 γ/ml, which for a sample weight of 5 g amounts to $2 \cdot 10^{-6}$%.

In taking polarograms for very dilute molybdenum solutions, the catalytic current is best expressed by applying the voltage during one revolution of the rheochord of 0.1 V, as can be seen from Fig. 10.

---

*In some experiments, when reduction of Mo^{VI} by ferrous sulfate occurred at higher temperatures, low values were obtained for the catalytic current as a result of partial reduction to Mo^{III}.

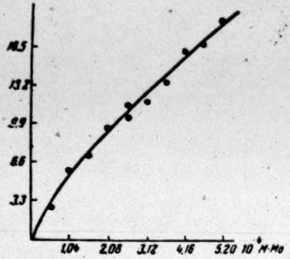


Fig. 8. Relation between the catalytic current of Mo and Mo concentration in a supporting electrolyte of 1 M $NaClO_4$ – 0.75 M H_2SO_4.

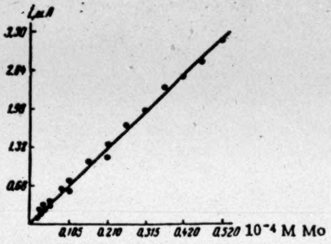


Fig. 9. Relation between the catalytic current of Mo and Mo concentration in a supporting electrolyte of 1 M $NaClO_4$ – 0.75 M H_2SO_4.

TABLE 3

Relation Between the Value of the Catalytic Current of Molybdenum and Its Concentration in 1 M $NaClO_4$ – 0.75 M H_2SO_4

Mo taken in γ/ml	Mo in M/l	i_k obtained in micro-amps	Mean i_k in micro-amps	$K = i_k/C$
10	$1.04 \cdot 10^{-4}$	5 83; 5.74	5.79	55.7
8	$8.3 \cdot 10^{-5}$	4.99; 4.99	4.99	60.1
5	$5.2 \cdot 10^{-5}$	3.16; 3.25	3.20	61.5
3	$3.1 \cdot 10^{-5}$	2.13; 2.16	2.15	69.3
2	$2.1 \cdot 10^{-5}$	1.33; 1.39	1.36	67.6
1	$1.04 \cdot 10^{-5}$	0.78; 0.80	0.79	76.0
0.8	$8.3 \cdot 10^{-6}$	0.67; 0.63	0.65	78.3
0.6	$6.2 \cdot 10^{-6}$	0.53; 0.53	0.53	85.4
0.5	$5.2 \cdot 10^{-6}$	0.45; 0.48	0.46	88.5
0.4	$4.2 \cdot 10^{-6}$	0.37; 0.39	0.38	90.5
0.3	$3.1 \cdot 10^{-6}$	0.29; 0.26	0.27	87.1
0.2	$2.1 \cdot 10^{-6}$	0.20; 0.19	0.19	90.5

Many elements have no effect on the catalytic current of molybdenum, since they do not form waves in a solution of 1M $NaClO_4$ – 0.75 M H_2SO_4; e. g. vanadium, chromium, tungsten, etc., do not interfere. Copper, bismuth, and iron, when present in appreciable amounts, have some effect. Iron can be reduced to Fe^{2+}. Nevertheless, during analysis of minerals, ores, and other natural objects, the amount of copper, iron, and bismuth, may be significant. Accordingly, it is best to separate molybdenum from other elements by extraction as the molybdenum-α-benzoinoxime complex with chloroform; during this process, it is also enriched.

4. Separation of Molybdenum from Fe, Cu, V, W, and Other Elements

In order to establish the completeness of separation of molybdenum by means of α-benzoinoxime from copper and other elements, synthetic mixtures were made up consisting of various amounts of molybdenum and other metals. To the solution was added 2 ml of a 2% alcoholic solution of α-benzoinoxime and the complex with molybdenum extracted with chloroform. Extraction was repeated twice again, and then, after evaporation of the chloroform on a warm hot-plate, and further treatment by the method described below, polarograms were taken from 0 to −0.6 V. The molybdenum content was then determined by means of a calibration curve. The results obtained are given in Table 4.

As is evident from Table 4, molybdenum can be determined in amounts of $1 \cdot 10^{-6}$-10^{-5} g by this method with satisfactory accuracy.

The method was used for determining molybdenum in granites, trondhjemites, skarns, and other rocks from the Tyrny-Auz deposits. Analysis was carried out as follows: an aliquot of the rock (1-2 g) was dissolved in

TABLE 4

Accuracy of Molybdenum Determination by Means of Its Catalytic Wave After Separating It from Other Elements by Extraction as Its Complex with α-Benzoinoxime

Mo taken in γ	Introduced in mg						Mo found in γ	Relative error in %
	Fe	Cu	Pb	Zn	V	W		
25	1.0	1.0	0.1	1.0	1.15	0.1	25.9	+3.6
10	1.0	1.0	0.1	1.0	1.15	0.1	10.8	+8.0
8	1.0	1.0	0.1	1.0	1.15	0.1	7.5	−6.2
5	1.0	1.0	0.1	1.0	1.15	0.1	5.1	+2.0
2	1.0	1.0	0.1	1.0	1.15	0.1	1.99	−0.5
1	1.0	1.0	0.1	1.0	1.15	0.1	0.92	−8.0
5	0.1	0.1	0.1	0.1	0.1	0.1	4.8	−4.0

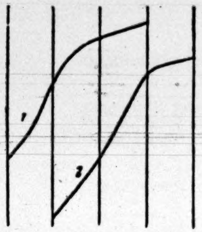


Fig. 10. $2.10 \cdot 10^{-5}$ M molybdate in a supporting electrolyte of 1 M $NaClO_4$ – 0.75 M H_2SO_4. Curve 1) potential drop of 0.2 V during one revolution of the drum; Curve 2) potential drop of 0.1 V during one revolution of the drum.

aqua regia, the solution evaporated down to 5 ml, cooled, and 2 ml of concentrated sulfuric acid added; the whole was then heated to the appearance of thick white fumes and then for a further 15-20 minutes. 20 ml of hot water was next added, the mixture boiled to dissolve the salts and the hot solution filtered free of deposit. The latter was washed 3-4 times on the filter with 0.5% sulfuric acid solution. Filtrate plus wash liquors were evaporated to a vaolume of ~. 10 ml and then neutralized with dry sodium carbonate till a precipitate appeared, this was dissolved by addition of 1-2 drops of sulfuric acid (1:1). The solution was transferred into a 50 ml separating funnel, and sulfuric acid added till its concentration was 1-2% (by volume) of the solution; this was followed by 2 ml of a 2% alcoholic solution of α-benzoinoxime and the whole shaken well; chloroform was next added and the mixture shaken for ~. 1 minute; after separation into layers, the chloroform layer was drained into a heat resistant 50 ml beaker. Extraction with chloroform was repeated a further two times, using 5 ml of chloroform each time; the extracts were evaporated on a hot plate to dryness and the residue calcined on a sand bath. An oxidizing mixture (2 ml concentrated H_2SO_4+ 5 ml concentrated HNO_3 + 5-10 drops of $HClO_4$) was added and the mixture heated till fuming ceased. To the hot solution 5 ml of supporting electrolyte was added (1 M $NaClO_4$ + 0.75 M H_2SO_4), hydrogen passed through the solution for 5 minutes and a polarogram registered from 0 to −0.6 V. The molybdenum content was determined by means of the calibration curve.

The results obtained are given in Table 5; Column 3 of this table contains the results of spectrographic analysis of the same rocks. Fig. 11 illustrates the molybdenum polarograms obtained for some of these rocks.

The results given in Table 5 show that there is good agreement between results of spectrographic and polarographic analysis respectively. The reproducibility of the analytical results for one sample is quite satisfactory (trondhjemites). The relative error does not exceed 5-6% for amounts of molybdenum of the order of 10^{-4}%.

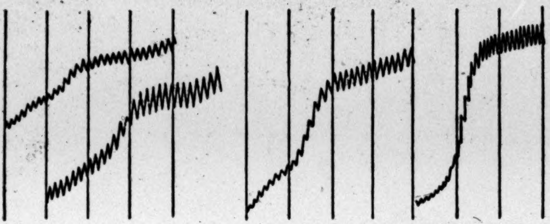


Fig. 11. Polarograms obtained for rock samples containing various amounts of molybdenum.

TABLE 5

Sample designation	Mo found in %	
	polarographically	spectrographically
Eldzhurtinsky granite	$7.35 \cdot 10^{-4}$	$6.3 \cdot 10^{-4}$
" "	$3.10 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$
" "	$2.80 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$
Leucocratic granite	$1.78 \cdot 10^{-2}$	$1.60 \cdot 10^{-2}$
Trondhjemite	$2.75 \cdot 10^{-3}$	$2.30 \cdot 10^{-3}$
Trondhjemite	$8.50 \cdot 10^{-4}$	—
"	$9.0 \cdot 10^{-4}$	—
"	$8.75 \cdot 10^{-4}$	—
Trondhjemite	$0.95 \cdot 10^{-3}$	—
"	$1.06 \cdot 10^{-3}$	—
"	$1.03 \cdot 10^{-3}$	—
"	$1.00 \cdot 10^{-3}$	—

SUMMARY

1. A study has been made of the catalytic wave of molybdenum in sodium perchlorate – sulfuric acid, and perchloric acid – sulfuric acid solutions respectively. It has been found that the limiting current of molybdenum in these media is independent of the pressure of the mercury column, and sulfuric acid concentration, but depends on perchloric acid concentration (or perchlorate), and, consequently, is kinetically determined.

2. It has been shown that the catalytic current of molybdenum is determined by re-oxidation of molybdenum (IV), obtained as the result of electrode reduction of Mo^V, by means of perchloric acid.

3. It has been established that in constructing a calibration curve it is possible to determine molybdenum quantitatively by means of its catalytic current down to amounts of $1 \cdot 10^{-6}$M with a relative error not exceeding ± 10%.

4. A method is suggested for determining molybdenum in rocks which is based on extraction of the complex formed between molybdenum and α-benzoinoxime with chloroform, and subsequent polarographic determination of molybdenum on the basis of its catalytic wave in a solution of sodium perchlorate – sulfuric acid or perchloric acid – sulfuric acid.

Received February 11, 1956.

LITERATURE CITED

[1] A. K. Babko and A. T. Pilipenko, Colorimetric Analysis (State Chem. Press, Moscow, 1951); Kh. G. Vinogradova, Collection, Methods for Determining Micro-Elements (Acad. Sci. USSR Press, 1950).

[2] S. I. Sinyakova, J. Appl. Chem. 10, 2109 (1937).

[3] K. B. Yatsimirsky and L. P. Afanasyeva, J. Anal. Chem. 11, 319 (1956) (T. p. 327).*

[4] Ya. P. Gokhshtein, J. Gen. Chem. 10, 1725 (1940); Trans. Commission on Analytical Chemistry Vol. II (V), 54, 1949; F. A. Uhl, Z. anal. Chem. 110,102 (1937); E. A. Kanevsky and L. A. Shvartsburg, Factory Lab. 9, 283, (1940).

[5] R. Pribil, and A. Blazek, Collection Czechoslov. Chem. Commun. 16, 561 (1953).

[6] I. M. Kolthoff, and E. P. Parry, J. Am. Chem. Soc. 73, 3718, 7228 (1951).

[7] I. M. Kolthoff, and E. P. Parry, J. Am. Chem. Soc. 73, 5315 (1951).

[8] A. Blazek and J. Koryta, Collection Czechoslov. Chem. Commun. 18, 326 (1953).

[9] N. Meiman, J. Phys. Chem. 22, 1454 (1948); J. Koutecky, Collection Czechoslov. Chem. Commun. 18, 311, 1953; A. G. Stromberg and L. M. Reinus, Trans. Commission on Analytical Chemistry, Vol. II (V), 34, 1949.

[10] M. C. Johnson, and R. J. Robinson, Anal. Chem. 24, 366 (1952).

[11] G. P. Haight, Anal. Chem. 23, 1505 (1951).

[12] G. B. Jones, Anal. Chim. Acta 10, 584 (1954).

---

*T. p. = C. B. Translation pagination.

BLANK
PAGE

COLORIMETRIC DETERMINATION OF NIOBIUM AND TANTALUM IN ORES

F. V. Zaikovsky

The All-Union Scientific Research Institute of Economic Mineralogy

Existing methods for individual determination of niobium and tantalum, which are based on the application of color reactions with pyrogallol [2, 6-9], and pyrocatechol [3, 5, 10], have considerable limitations because of interference from titanium.

Titanium in oxalate solution, just like niobium and tantalum, forms a most intensely colored pyrogallate or pyrocatechinate, on the yellow background of which it is impossible to determine niobium and tantalum colorimetrically.

Separation of either large or small amounts of titanium from niobium and tantalum by means of tannin is not quantitative. Even when precipitation is repeated two or three times, traces of titanium, sufficient to interfere with the colorimetric determination of the other two metals, are still not removed from niobium and tantalum. Application of corrections for the titanium content during determination of hundredths or even thousandths of a percent of niobium and tantalum, lead to large errors, or exclude determination.

In the work described in the present article, we used as a basis extraction separation of niobium, tantalum, and titanium which we have described previously [1]. Using this principle we have developed a colormetric method for determining niobium and tantalum in ores.

Principle of the Method

Niobium, tantalum, and certain other elements, in oxalate solution, and depending on pH, can form complex compounds with pyrocatechol (ortho-dihydroxybenzene). The pyrocatechinates of niobium, tantalum, and titanium, at different pH values of the oxalate solution, transfer from an aqueous phase into a n-butanol phase.

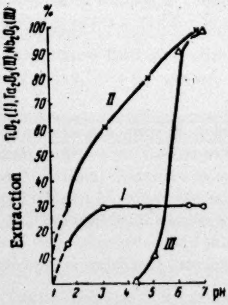


Fig. 1.

Only three elements – niobium, tantalum, and titanium – are extracted at a different pH value as the pyrocatechinates. Other elements (iron, zirconium, tungsten, aluminum, etc.) are not extracted and do not interfere with extraction of niobium and tantalum.

The distribution of niobium, tantalum, and titanium in relation to pH of the oxalate solution, for equal phase ratios, using a concentration of 5%, and an element concentration of 0.5 mg/ml (calculated as the oxide) is shown in Fig. 1.

From Fig. 1 it can be seen that at a pH of 7, niobium and tantalum are quantitatively extracted, while titanium is only extracted to the extent of 30%. If the extracted niobium, tantalum, and titanium are transferred back into the oxalate solution (after removal of alcohol and precipitation with cupferron) and extraction of the pyrocatechinates with n-butanol carried out at pH 3, then, as can be seen from Fig. 1, titanium and tantalum are separated from niobium. On treating the extract with dilute sulfuric or hydrochloric acid, titanium is re-extracted into the aqueous phase, while tantalum remains in the extract [1]. Tantalum transfers from the alcohol solution into the oxalate solution and is determined colorimetrically.

As a result of these operations, titanium is separated from niobium and tantalum, and at the same time niobium is separated from tantalum.

Niobium and tantalum can be determined colorimetrically with pyrogallol or pyrocatechol. Pyrogallol, when compared with pyrocatechol, is a more sensitive reagent for niobium and tantalum, but since it is readily oxidized, while the pyrogallates of niobium and tantalum are more difficult to extract with n-butanol, it is not really expedient to use it. The optimum concentration of pyrocatechol or pyrogallol in the solution to be measured colorimetrically should be 4-5%. Colorimetric measurements can be carried out by the standard series method, or on a photocolorimeter (niobium).

Niobium in oxalate media at a pH of 7-8 forms a yellow complex with pyrocatechol and pyrogallol which can be extracted with n-butanol. It is best to carry out colorimetric measurements on niobium at a pH of 7, since at this pH the color of the complex is most stable. Tantalum in an oxalate medium which is slightly acid forms a yellow complex with a greenish tinge with pyrocatechol and pyrogallol.

Traces of titanium, if not removed completely, interfere with colorimetric determination of niobium and tantalum. Solutions of titanium pyrogallate and titanium pyrocatechinate respectively in acid media, have a yellowish-orange color, while in weakly alkaline media, the color is yellow with a greenish-yellow shade.

Preparation of Reagents

1. Standard niobium and tantalum solution containing 0.1 mg/ml of the pentoxides of niobium and tantalum, respectively. 10 mg of the pentoxides of niobium and tantalum, respectively, are slowly fused with 1.5 g of potassium pyrosulfate. The cooled melt is dissolved on heating in a 3% solution of ammonium oxalate, and after cooling transferred to a standard flask where it is made up to 100 ml with ammonium oxalate solutions.

2. 20% pyrocatechol solution; to 50 ml of the solution is added 2 ml of a 15% solution of stannous chloride in 10% (by volume) hydrochloric acid. This solution can be kept for 5-6 days.

Analytical Procedure

Dissolving the rare earth acids in oxalate solution. 0.1-1 g of the ore is heated in a platinum basin first with hydrogen fluoride and then with sulfuric acid (5 ml HF and 10 ml H_2SO_4); the residue is calcined and fused with 10-12 times its amount of potassium pyrosulfate. The melt is dissolved on heating in 25 ml 3% ammonium oxalate, and, after cooling, filtered. Residue + filter are placed in the original platinum basin and dried, calcined, and then fused with 0.5-0.6 g of potassium pyrosulfate, the melt dissolved in 10-15 ml ammonium oxalate, and the filtered solutions combined.

If the ores contain large amounts of titanium (more than 5-6 mg in the aliquot) then in order to remove the bulk of the titanium, the aliquot is heated in the platinum basin with hydrogen fluoride and sulfuric acid.

After removal of the acids the residue is calcined; 15 ml of concentrated hydrochloric acid is added and the mixture evaporated to half volume. The contents are transferred to a 500 ml beaker with the help of 300 ml 1% tannin solution in 10% (by volume) hydrochloric acid and some filter aid (macerated filter paper) added. The liquid is boiled for 30 minutes and, on the following day, filtered. The filtrate is discarded.

Precipitate + filter after washing with a dilute tannin solution are transferred to a crucible, dried, calcined, and fused with 0.5-0.6 g potassium pyrosulfate. The melt is dissolved on heating in 25 ml of ammonium oxalate solution.

Extractive separation of niobium and tantalum from accompanying elements. Pyrocatechol in an amount equivalent to 6% of the volume of the solution is dissolved in the oxalate solution obtained, which contains niobium, tantalum, titanium and other elements; ammonia solution is added dropwise, and, towards the end, a saturated solution of sodium sulfite, till the solution darkens (reaction with iron); then a further 5 ml added (pH 7-8). The solution is transferred to a 100 ml separating funnel, and, after 10 minutes, 12-15 ml butanol saturated with water added, and the whole shaken for 20-25 seconds. After the layers have separated, the lower aqueous layer is transferred into another funnel and repeatedly extracted with 8-10 ml butanol.

The combined extracts are transferred to a porcelain basin and evaporated to dryness on a water bath, 15-20 ml of water is added to the residue and it is again evaporated almost to dryness, it is then dissolved on heating in 20-30 ml of 10% sulfuric acid; after cooling, 8-10 ml of 3% cupferron solution is added and the whole mixed. After 2-3 minutes, the cupferronates are filtered off using filter aids; filter + precipitate are transferred to a crucible, carefully dried, and calcined.

Extractive separation of niobium, tantalum, and titanium. The calcined residue, containing niobium, tantalum, and some titanium is fused with 0.3-0.4 g potassium pyrosulfate; the cooled melt is dissolved on heating in 22-25 ml ammonium oxalate, the solution cooled, and sodium sulfite solution or dilute sulfuric acid added to adjust the pH to 2.5-3 with respect to Congo; this operation should be carried out with care, since on lowering the pH to 2, extraction of titanium as the pyrocatechinate is difficult, while at pH greater than 4, appreciable amounts of niobium are extracted. After fixing the pH, 4 g of pyrocatechol is dissolved in the solution which is then transferred to a separating funnel, 8-10 ml of butanol is added, and the whole shaken for 20-25 seconds. When the layers have separated out, the aqueous layer is transferred to another funnel and extraction with butanol repeated. If, during extraction, the volume of the oxalate solution decreases, it should be made up to the original volume.

After 4-5 extractions, the oxalate solution should be completely colorless indicating quantitative removal of titanium. The last extraction with n-butanol should be carried out with addition of pyrocatechol. After extractive separation of titanium and tantalum, the oxalate solution containing niobium is transferred to a 25 or 50 ml flask, made up to the mark with a solution of ammonium oxalate and colorimetric measurements made (see determination of niobium).

The extract (the first three combined extracts) containing tantalum and titanium is treated in a separating funnel, 2-3 times, with 10-15 ml of 3% (by volume) sulfuric acid to remove titanium pyrocatechinate. After the last extraction, the aqueous phase should be colorless, or only have a weak yellow color, thereby indicating almost complete separation of titanium (aqueous phase) from tantalum (extract).

The extract is evaporated on a water bath, and to the residue 20 ml of water is added, the mixture is again evaporated almost to dryness; this residue is then dissolved on heating in 10-20 ml of 10% sulfuric acid, 1 ml of a 1% solution of a zirconium salt added, and, after cooling, 8-10 ml cupferron solution added. The precipitate is filtered, transferred to a crucible, dried, calcined, and the residue fused with 0.2-0.3 g of potassium pyrosulfate.

The melt is dissolved in 20 ml of ammonium oxalate solution on heating; 1 g of pyrocatechol is added, and after fixing the pH at 7-8 (using indicator or litmus paper) the solution is transferred to a 50 ml separating funnel and the tantalum pyrocatechinate extracted once with 8-10 ml n-butanol.

The extract is treated 2-3 times with 5-6 ml of 3% sulfuric acid, and the solution evaporated on a water bath; 15-20 ml of water is then added to the residue and the mixture evaporated almost to dryness again. The residue is finally dissolved on heating in 10-20 ml sulfuric acid, 1 ml of a solution of a zirconium salt added, and, after cooling, 8-10 ml cupferron solution added. The cupferronates are filtered off, transferred to a crucible, dried, and calcined; the final residue is fused with 0.2-0.3 g potassium pyrosulfate.

The cooled melt is dissolved on heating in 5-10 ml ammonium oxalate and the tantalum determined colorimetrically.

Determination of Niobium

Colorimetric determination of niobium can be carried out on a photocolorimeter and by the method of standard series (scales).

Photocolorimetric determination. 0.5-5 ml of test solution and 2 ml of pyrocatechol solution are introduced into a 10 ml measuring cylinder and the whole mixed. No yellow color should appear when this is done, thereby indicating complete separation of titanium. 1-3 ml of a saturated solution of sodium sulfite is added, and the volume made up to 10 ml with a 3% solution of ammonium oxalate; the whole is mixed, and after 5-6 minutes the optical density of the solution measured using a blue light filter and a layer thickness of 10 mm. A standard series is prepared by introducing 0, 10, 20, 30 . . . γ niobium into 10 similar cylinders, and the reagents indicated added. The solutions are mixed and the optical density measured after 5-6 minutes, as indicated above; a calibration curve is then drawn (Fig. 2).

Determination by the method of a standard series. Into a 10-12 ml test tube of colorless glass is introduced 0.5-3 ml of test solution, 1 ml of pyrocatechol solution (pyrogallol), 1-2 ml of sodium sulfite and the whole mixed.

Reference solutions are prepared by introducing into 3-4 similar tubes different amounts of a standard niobium solution, 1 ml of pyrocatechol solution, and 1 ml of saturated sodium sulfite solution; the volumes of the reference and test solutions respectively are levelled up with ammonium oxalate solution, mixed, and measured colorimetrically after 5-6 minutes.

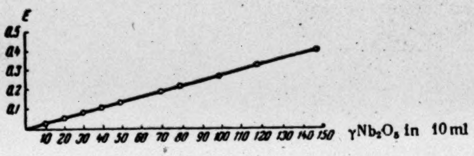


Fig. 2.

Determination of Tantalum

Into a similar test tube is introduced 1-3 ml of test solution,* 0.5 ml of a 5% solution of sulfuric acid, 1 ml of pyrocatechol solution (pyrogallol) and the whole mixed.

Reference solutions are prepared in the same way by introducing various amounts of a standard solution of tantalum into 5-6 test tubes, followed by 0.5 ml of a 5% solution of sulfuric acid, 1 ml of pyrocatechol (pyrogallol) solution, and the volumes in the test tubes made up to the same level (5 ml) with ammonium oxalate solution; the solutions are mixed and neasured colorimetrically. The solutions can be kept in the dark without change in color for 5-6 days.

Comparison of the results obtained by the two methods, as is evident from the tables, show satisfactory agreement and reproducibility. Sometimes, it is not possible to get results when the tannin-pyrogallol method [2, 7-9] is used, particularly for large titanium contents. There are a few variants of this method. If precipitation of niobium and tantalum with tannin is carried out from a 25% (by volume) hydrochloric acid solution [11], then, in many cases, titanium is more completely separated and satisfactory results can be obtained. Niobium and tantalum can be precipitated with tannin from sulfuric acid media also.

Mineral raw materials are analyzed with less difficulty, when the titanium content does not exceed the niobium and tantalum contents. It is important to take into account not the total titanium content of the ore (e. g. 10, 20, 30%), but its quantitative relationship to niobium and tantalum.

If, e. g., the ore contains 20% titanium, 1% niobium, and 0.02% tantalum, then the ratio of niobium and tantalum to titanium is 1:20, which is more favorable for analysis than e. g. a case where the ore contains 0.05% niobium, 0.003% tantalum, and 20% titanium (ratio of Nb:Ti = 1:400).

The method of determining niobium and tantalum is applicable to the ores most commonly met, which are subjected to acid decomposition. Ores containing tin in the form of cassiterite or other forms which are sparingly soluble, are not decomposed by acids, and in order to get niobium and tantalum into the oxalate solution, some preliminary operations are necessary: decomposition of the sample, e. g. with potassium difluoride, and after removal of the fluoride ion, precipitation of niobium and tantalum with tannin.

Exceptions are, in general, comparatively rare in chemical laboratory practice, and do not lead to exceptional difficulties during determination of niobium and tantalum.

If the ore or mineral contains small amounts of titanium and iron (0.1-0.5%), then it is possible, in many cases, to simplify the analytical procedure described.

After getting niobium and tantalum into oxalate solution, traces of iron are reduced by adding 2-3 ml of a 10% solution of stannous chloride and 10% hydrochloric acid; titanium and tantalum are separated from niobium at a pH of 3 and the procedure already described then followed.

---

*To another aliquot is added, beforehand, 1 ml of dilute sulfuric acid, 2-3 drops of hydrogen peroxide, and, in cases where traces of titanium are present, (not exceeding 5-6 γ), titanium is also added to the reference solution in exactly equivalent amounts (for compensation).

TABLE

Determination of Niobium and Tantalum in Ores*

Test material	Found in %					
	by the given method			by the tannin-pyrogallol method		
	sample wt. in g	Nb_2O_5	Ta_2O_5	sample wt. in g	Nb_2O_5	Ta_2O_5
Synthetic mixture № 1 TiO_2 — 10% Nb_2O_5 — 0.01% Ta_2O_5 — 0.05% . .	0.25	0.012 0.011	0.04 0.05	—	—	—
Synthetic mixture № 2 TiO_2 — 1.5% Nb_2O_5 — 0.05% Ta_2O_5 — 0.32% . .	0.50	0.052 0.060	0.30 0.36	— —	—	—
Ore (TiO_2 10%)	0.050	11.0 10.8	0.12 0.12; 0.13	0.25	10.8	0.12
KO № 1 (TiO_2<0.5%) . . .	0.5—1.0	0.014 0.010 0.012 0.010	0.009 0.009 0.012	2—3.0	0.012	0.01
KO № 2 (TiO_2—8.0%) . . .	0.25	0.06 0.062 0.08 0.066	0.006 0.006	0.50	0.07	0.008
Ore (TiO_2—0.5%) . . .	1.0	0.050 0.055 0.060	0.005 0.006 0.006	2--3.0	0.06	—
Ore (TiO_2 — 0,1%) . .	1.0	0.011 0.010 0.012	0.006 0.007	—	—	—
Ore (TiO_2 — 0,2%) . .	1.0	0.006; 0.005 0.006; 0.006	0.006 0.006 0.006 0.007	3.0	0.004	0.005
Ore (TiO_2 1,6%) . . .	0.25	0.23; 0.27	0.05 0.06	1.0	0.24	0.06
Ore (TiO_2 0,6%) . . .	0.2	0.44; 0.43 0.44	0.09; 0.08 0.08	1.0	0.44	0.08

---

*The following chemists participated in the ore analysis: S. Ya. Kamentsev, M. P. Kiselev, M. I. Medvedev, V. I. Sergeev, L. M. Kulakova, and G. I. Nikitina.

TABLE (continued)

Test material	Found in %					
	by the given method			by the tannin-pyrogallol method		
	sample wt. in g	Nb_2O_5	Ta_2O_5	sample wt. in g	Nb_2O_5	Ta_2O_5
Concentrate (TiO_2—48%) . . .	0.1	1.05; 1.00 1.02	0.020 0.020 0.018	—	—	—
Ore (TiO_2—17%) . . .	0.2	0.36; 0,32	—	0.20	0.40	—
Ore (TiO_2—43%) . . .	0.1	0.88; 0.92	0.005 0.006	0.20	0.92	—
Ore (TiO_2 — 44%) . . .	0.1	0.69	0.005	0.20	0.60	—
Ore. (TiO_2—0.3%) . . .	0.5	0.12; 0.11	0.002 0.003	0.50	0.12	—
Ore (TiO_2—0.2%) . . .	0.5	0.50	0.003	0.50	0.50	0.003
Ore (TiO_2—0.2%) . . .	1.0	0.042	0.003	2.0	0.040	0.004

In other cases, when it is necessary to determine one of the elements, either niobium or tantalum, it is possible to cut down the procedure. In the residue, after separation of niobium, tantalum, and some of the titanium, niobium is determined by the thiocyanate method [4].

To determine tantalum alone in the ore, it is necessary to extract it as the pyrocatechinate from oxalate solution at a pH of 7, and then, after re-extraction of the titanium, it is determined with pyrocatechol or pyrogallol. One such determination takes 6-8 hours if no complicated operations are involved.

SUMMARY

A method has been developed for the colorimetric determination of niobium and tantalum in ores, using pyrocatechol or pyrogallol, after extractive separation of niobium, tantalum, and titanium.

The capacity of the pyrocatechol complexes of niobium, tantalum, and titanium to be extracted by n-butanol at differing pH values in oxalate solutions is the basis for the separation.

The method has been checked on various ores.

Received January 11, 1956.

LITERATURE CITED

[1] F. V. Zaikovsky. J. Anal. Chem. 11, 269 (1956) (T. p. 277).*

[2] N. F. Krivoshlykov and M. S. Platonov, Trans. All-Union Conference on Analytical Chemistry, Vol. 2, 359 (1943).

[3] Yu. V. Karyakin and M. P. Telezhnikova, J. Appl. Chem. 19, 4, 435 (1946).

[4] I. P. Alimarin and R. L. Podvalnaya, J. Anal. Chem. 1, 30 (1946).

[5] O. Tomicek, and L. Jarman, Chem. Listy 46, 3, 144 (1952).

[6] E. C. Hunt, and R. A. Wells, Analyst 79, 939, 345 (1954).

[7] G. Norwitz, M. Codell, and I. I. Mikula, Anal. Chim. Acta 11, 173 (1954).

[8] I. I. Dinnin, Anal. Chem. 25, 12, 1803 (1953).

[9] N. F. Krivoshlykov and M. S. Platonov, J. Appl. Chem. 10, 184 (1937).

[10] O. Tomicek, K. Spurni, L. Jarman, and V. Holecek, Collection Czechoslov. Chem. Commun. 18, 6, 757 (1953).

[11] A. P. Bocharova, Bull. All-Union Inst. Mineral Raw Materials 6, 158, 1956.

---

*T. p. = C. B. Translation pagination.

BLANK
PAGE

APPLICATION OF TRIHYDROXYFLUORONE DERIVATIVES IN COLORIMETRIC ANALYSIS

DETERMINATION OF ANTIMONY

V. A. Nazarenko and N. V. Lebedeva

In one of our previous articles [1], we described 16 derivatives of 2, 3, 7-trihydroxy-6-fluorone, substituted in position 9, which are highly sensitive reagents for detecting antimony. In the same article we also briefly discussed the conditions for using 9-phenyl-2, 3, 7-trihydroxy-6-fluorone (phenylfluorone) for the colorimetric determination of this metal. In the present article the use of phenylfluorone as a reagent for colorimetric determination of antimony is studied in greater detail.

Phenylfluorone was synthesized from triacetylhydroxyhydroquinone and benzaldehyde [2]; during this synthesis it was found that it was possible to take only double the theoretical amount of benzaldehyde without decreasing the yield of phenylfluorone. The use of such a large amount of benzaldehyde as was used for the synthesis by Gillis and coworkers [2], only contaminates the reagent with resinous products of the decomposition of excess aldehyde. Purification of phenylfluorone was carried out through its sulfate by crystallization from ethyl acetate and sulfuric acid [3]. 0.05 and 0.032% solutions ($1.56 \cdot 10^{-3}$ and $1 \cdot 10^{-3}$ M) were used in the work, for the preparation of which, 50.0 or 32.0 mg of phenylfluorone dried at 105° was dissolved on slight heating in 90 ml of 95% ethanol and 0.5 ml of 6N hydrochloric acid, and, after cooling the solution diluted with ethanol in a standard flask to 100 ml.

Phenylfluorone, in acid solution, forms a red colored precipitate with trivalent antimony. For low antimony concentrations the precipitate remains in solution in the form of a suspension which is easily stabilized by gelatin. When this is done the solution remains transparent. The color of solutions stabilized by gelatin changes from a pure yellow (the color of an acid solution of the reagent itself) through an intermediate orange color to a red when excess antimony is present.

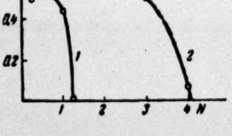


Fig. 1. Effect of acidity on color development: 1) HCl; 2) H_2SO_4.

Effect of acidity. For low acidity (pH > 1) a fine crystalline precipitate of the reagent forms. On carrying out reactions for antimony in solutions with acidity below 0.2 N, a precipitate of the antimony compound separates out rapidly even in the presence of gelatin. At acidities of 0.2 N and higher, the solutions remain transparent, while at acidities greater than 0.5 N formation of color slows down to greater extents, the higher the acidity of the solution. On Fig. 1 is shown the relation between color intensity and acidity. The solutions were $1.6 \cdot 10^{-5}$ M with respect to antimony, $4 \cdot 10^{-5}$ M with respect to phenylfluorone, and contained gelatin (2 ml of 1% solution in a total volume of 50 ml). Measurements were carried out on a Pulfrich photometer in a 10 mm cell, against water, at a wave-length of 530 millimicrons, 3 hours after preparing the solutions. All further measurements were also carried out on the Pulfrich photometer.

When sulfuric acid was used, variations in acidity from 0.2 to 2.5 N (after standing it for long enough) had no effect on color intensity (Fig. 1); at acidities greater than 2.5 N, color intensity dropped rapidly. When hydrochloric acid was used a sharp decrease in color intensity was observed even at acidities greater than 0.75 N.

One might think therefore that at very low (10^{-5} M) antimony concentrations in weakly acid solution, antimony is present in the form of SbO^+ ions which react with phenylfluorone. On increasing the acidity Sb^{3+} ions which do not react with phenylfluorone begin to predominate; this is reflected on the curve relation color intensity to acid concentration by a sharp drop. The effect of acidity is expressed more sharply in hydrochloric acid solutions than in sulfuric acid solutions, because of the lower activity coefficient of sulfuric acid, and the high stability of the chloro complexes of antimony. Subsequent work was therefore carried out with 1 N sulfuric acid solutions.

Composition of the complex. Although antimony forms an insoluble compound with phenylfluorone, thanks to the fact that colloidal solutions of this compound are readily stabilized by gelatin, it was found possible to use optical methods for determining the ratio of Sb : phenylfluorone in the complex. For this purpose the continuous change method of Ostromyslensky-Job, and the method of molar ratios [4] were used. In addition, use was made of the method of molar extinction coefficients of Tolmachev [5].

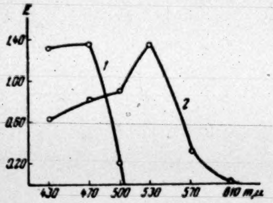


Fig. 2. Absorption curves: 1) Phenylfluorone; 2) antimony complex.

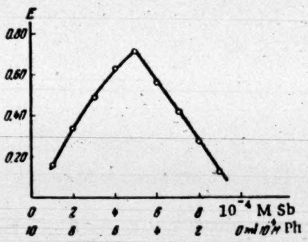


Fig. 3. The method of continuous changes.*

Absorption curves of solutions of reagent and of the antimony complex respectively were taken. The solutions were $4 \cdot 10^{-5}$ M with respect to phenylfluorone, while in the case of the complex it was $6 \cdot 10^{-5}$ M with respect to antimony. 2 ml of 1% gelatin was added per 50 ml solution. This amount of gelatin was used in all subsequent experiments. Measurements were carried out in a 10 mm cell against water. Absorption curves are shown on Fig. 2; from these it is clear that a sharp absorption maximum is observed for the antimony complex at 530 mμ, where reagent solutions do not show any absorption at all. This wave-length was chosen for further work.

Solutions for taking measurements according to the method of continuous changes were prepared as follows: to 1-9 ml of $4 \cdot 10^{-4}$ M $SbCl_3$ in 0.1 N hydrochloric acid was added 20 ml of 2.5 N sulfuric acid, 2 ml of gelatin solution, the whole mixed, and 9-1 ml of $4 \cdot 10^{-4}$ M alcoholic solution of phenylfluorone, obtained by diluting $1 \cdot 10^{-3}$ M solution, added. In order to maintain alcohol concentration constant in all cases, the alcohol added was such that the total volume of phenylfluorone and alcohol was 9 ml. After mixing, the solutions were diluted with water to 50 ml. Solutions prepared in this way were $0.8 \cdot 10^{-5}$ to $7.2 \cdot 10^{-5}$ M with respect to antimony, and $7.2 \cdot 10^{-5}$ to $0.8 \cdot 10^{-5}$ M with respect to phenylfluorone. Optical density measurements were made in a 10 mm cell against water, 5 hours after making up the solutions. Standing for 5 hours was found to be adequate. Keeping the solutions for 6, 10, and 20 hours did not lead to any changes in extinction values. Results are shown on Fig. 3.

Solutions were prepared in a similar manner for use in the method of molar ratios. Phenylfluorone concentration was kept constant at $4 \cdot 10^{-5}$ (2 ml of $1 \cdot 10^{-3}$ M solution), while antimony concentration was changed from 0.4 to $8 \cdot 10^{-5}$ M (1-20 ml of $2 \cdot 10^{-4}$ M solution). No additional alcohol was added. Optical density measurements were made in a 10 mm cell against water, also 5 hours after making the solutions up. Results are given in Fig. 4.

In Tolmachev's method, molar extinction coefficients obtained by the "saturation" method at a fixed antimony concentration and excess of phenylfluorone on the one hand, were compared with those obtained at a fixed concentration of phenylfluorone and excess antimony on the other (results are given in Table 1). The molar extinction coefficient in each case was found to be 34000 and the ratio

---

* Ph = phenylfluorone.

$$\frac{\varepsilon_{Sb}}{\varepsilon_{Ph}} = 1.$$

Thus, experimental results of all the three optical methods point to the formation of a complex with a ratio of Sb:phenylfluorone = 1:1. This agrees with the results of Wenger and coworkers [6], who studied the composition of the complex formed between antimony and methylfluorone, and found gravimetrically a ratio of Sb:methylfluorone of 1:1.

The structure of antimony phenylfluoronate can be represented by Formula (I), taking into account the results obtained above, and also bearing in mind that the reactive group of atoms in phenylfluorone, as in other 2, 3, 7-trihydroxy-6-fluorones, is orthoquinonoc. This group is also present in other reagents which give colored compounds with trivalent antimony and germanium (azo derivatives of pyrocatechol and the tautometic hydrazo form, hematein, purpurogallin, and chloranilic acid). The structure of antimony methylfluoronate (II), proposed by Wenger [6] in which he ignores the presence in the methylfluorone of the ortho-hydroxyquinone group is not correct in our opinion.

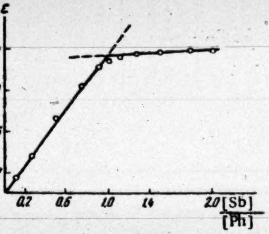
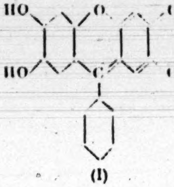
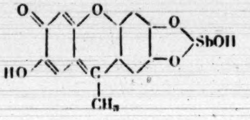


Fig. 4. Method of molar ratios.



(I)



(II)

Molar extinction coefficient, equilibrium constant. Molar extinction coefficient was determined by the "saturation" method. It is clear from Fig. 5 that double the theoretical amount of phenylfluorone is already sufficient for complete complexing of the antimony, while, as can be seen from Experiment No. 5, Table 1, this amount may be even less. In the same way, from Fig. 4, it is clear that 1.5 times the amount of antimony is already sufficient for complexing all the phenylfluorone. Experiments were carried out at various antimony concentrations and a constant phenylfluorone concentration, and vice-versa; solutions, were, as usual, 1 N with respect to sulfuric acid, and contained gelatin. The equilibrium constant of the reaction:

$$SbO^+ + HPh \rightleftharpoons SbOPh + H^+ \tag{1}$$

was calculated from the ratio of the optical density of solutions of the complex at stoichiometric ratios of antimony and phenylfluorone, and of solutions containing excess of one of the components. Designating in Equation (1) the equilibrium concentration of the complex [SbOPh] x, and the equilibrium concentrations of antimony and phenylfluorone [SbO⁺] = [Ph] = (1 − x), we get

$$K = \frac{x}{(1-x^2)}. \tag{2}$$

TABLE 1

Determination of the Molar Extinction Coefficients and Equilibrium Constant

(l = 10 mm; t = 19°; time of standing 5 hours)

Expt. No.	$c_{Sb}\cdot 10^6$	$c_{Sb} = c_{Ph}$		$c_{Sb} \ll c_{Ph}$		ε	pK
		$c_{Ph}\cdot 10^6$	E	$c_{Ph}\cdot 10^6$	E_{max}		
1	1.6	1.6	0.495	8	0.545	34060	6.84
2	2.4	2.4	0.76	8	0.82	34170	6.88
3	3.2	3.2	1.03	8	1.10	34380	6.86
4	4.0	4.0	1.29	8	1.36	34000	—
5	4.8	—	—	8	1.65	34370	—
6	6.0	—	—	4	1.36	34000	6.95
					Mean	34160	6.88

The value of [H⁺] can be ignored in the given instance, since the reaction is carried out at high acidity, while the molar concentrations of the reactants are very small (10^{-5} M). Taking into account the fact that for excess of one of the components that x = c, where c is the initial concentration of the second component, we have

$$\frac{x}{c} = \frac{E}{E_{max}} \text{ and } x = \frac{Ec}{E_{max}}, \qquad (3)$$

where E is the optical density at stoichiometric ratios of the components, while E_{max} is the same for excess of one of the components.

The values obtained for the molar extinction coefficient (ϵ) and pK (logarithm K) are given in Table 1.

The equilibrium constant and molar extinction coefficient were also calculated by Komar's method [7, Formulas 10a and 11a]. For this purpose use was made of results of measurements of optical density of solutions of the complex at stoichiometric ratios of antimony and phenylfluorone; these values are given in Table 1 (Experiments 1, 2, and 3). The values obtained are given in Table 2.

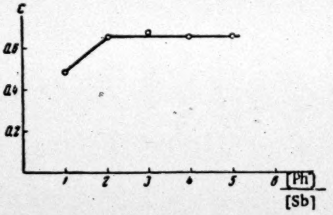


Fig. 5. Effect of excess reagent on color intensity.

It is evident from Table 2, that the values of ϵ and pK, obtained by means of Komar's method, are in agreement with the values obtained for these constants by means of the first method of calculation using the "saturation" method. In the given instance preference is given to the values obtained by the first method of calculation, since, in the case of stable complexes, of which the antimony complex with phenylfluorone is an example the "saturation" method gives more accurate results.

The high value of the molar extinction coefficient characterizes the method as a very sensitive one. The large value of the equilibrium constant indicates that the antimony complex of phenylfluorone is very stable. This constant can be used for calculating the necessary excess of reagent. Calculation shows that in order to complex 90% of the antimony as a colored complex, a 1.6 fold excess of phenylfluorone is sufficient. This agrees with the results given in Fig. 5.

TABLE 2

Determination of the Molar Extinction Coefficient and Equilibrium Constant by Komar's Method

Combination of experiments	ε	pK
1-2	35130	6.59
1-3	35110	6.52
2-3	35810	6.42
Mean	35350	6.51

Effect of time. Using a large excess of phenylfluorone in 0.2-1.5 N sulfuric acid, the maximum color develops within 15 minutes and does not change in the course of many hours. On long standing (during the second 24 hours) a red film of complex starts to settle out on the glass.

Conformation with Beer's law. In order to ascertain whether or not stabilized solutions of the antimony phenylfluorone complex follow Beer's law, the optical density of solutions containing the following amounts of antimony $0.04 \cdot 10^{-5}$ M (0.049 γ/ml) to $4.8 \cdot 10^{-5}$ M (5.8γ/ml) was determined at a constant phenylfluorone concentration of $8 \cdot 10^{-5}$ M. Measurements were made against a blank (a similar solution free from antimony) in 50, 10, and 5 mm cells. The results obtained are represented on Fig. 6, from which it is clear that within the concentration limits studied, there is a linear relationship betweeen color intensity of the solution and antimony concentration. On increasing the antimony concentration beyond $5 \cdot 10^{-5}$ M, the colors obtained are too intense and a film of complex is rapidly deposited on the cell walls.

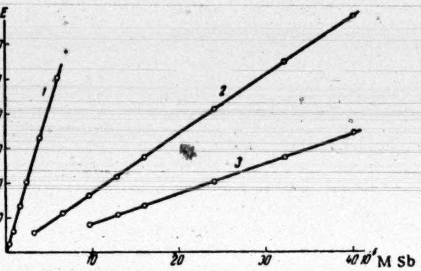


Fig. 6. Relation between color intensity and antimony concentration: 1) 50 mm, 2) 10 mm, 3) 5 mm.

Recommended procedure for antimony determination. Into a 25 ml standard flask is measured a weakly acid (hydrochloric or sulfuric acid) test solution, such that, after dilution to the mark, antimony concentration is within the limits of 0.05-6γ/ml. 10 ml of 2.5 N sulfuric acid and 1 ml of 1% gelatin solution are then added, the whole mixed and 2.5 ml of a 0.03% phenylfluorone solution added. The solution is again mixed, diluted to the mark with water, and left for 15-30 minutes, after which optical density measurements are made using a light filter with maximum transmission at 530 mμ against a blank in a suitable cell. It is also possible to use other volumes, 5-10-50 ml; the ratio of reagents, and the order in which they are added must however be the same as before. Color intensity can also be measured by means of a series of standards.

The use of other trihydroxyfluorone derivatives. Other trihydroxyfluorone derivatives described in article [1], can also be used as well as phenylfluorone for colorimetric determination of antimony. In particular, good results can be obtained by means of 9-(p-nitrophenyl)-2, 3, 7-trihydroxy-6-fluorone, the complex of which with antimony exhibits maximum absorption in the 570 mμ region, in contrast to phenylfluorone and other tested trihydroxyfluorone derivatives, whose antimony complexes show maximum absorption in the 530 mμ region. These other derivatives have no advantages over phenylfluorone, and are not so readily accessible or so easily prepared.

SUMMARY

The use of phenylfluorone as a reagent for colorimetric determination of antimony has been studied spectrophotometrically. Phenylfluorone forms a complex with antimony which has a ratio of Sb: phenylfluorone of 1:1. The probable formula of antimony phenylfluoronate is given. The absorption maximum of the complex lies at 530 mμ, its molar extinction coefficient is 34160, and equilibrium pK is 6.88. Solutions of the complex stabilized by gelatin obey Beer's law. Colorimetric determination is possible in the antimony concentration range of 0.05 to 6γ/ml. A procedure for determining antimony is outlined.

Received January 26, 1956.

LITERATURE CITED

[1] V. A. Nazarenko and N. V. Lebedeva, J. Anal. Chem. 10, 289 (1955) (T. p. 273).*

[2] J. Gillis, J. Hoste, and A. Claeys, Anal. Chim. Acta 1, 302 (1947).

[3] C. Liebermann, and S. Lindenbaum, Ber. 37, 1171 (1904).

[4] J. H. Yoe, and A. L. Jones, Ind. Eng. Chem., Anal. Ed. 16, 111 (1944).

[5] V. N. Tolmachev, Sci. Proc. Kharkov University 54, 83 (1954).

[6] P. Wenger, R. Duckert, and C. P. Blancpain, Helv. Chim. Acta 20, 1427 (1937).

[7] N. P. Komar, J. Anal. Chem. 5, 139 (1950).

---

*T. p. = C. B. Translation pagination.

CHROMATOGRAPHIC SEPARATION OF RADIOELEMENTS OF THE YTTRIUM GROUP OF ELEMENTS OBTAINED DURING FISSION OF YTTERBIUM AND HAFNIUM BY HIGH ENERGY PROTONS

A. A. Pozdyakov

V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry

In connection with intensive development of work on radiochemical studies of nuclear transformations occurring under the influence of high energy particles, the study of the nature of the residual nuclei in the field of rare earth elements is of considerable intesest, both from the point of view of searches for new isotopes and for determining the yield of individual isotopes. It was essential to find a rapid and effective method of separating various nuclei of the radioisotopes of rare-earth elements formed during fission.

The most efficient method of separating ultra-small amounts of rare-earth elements is ion-exchange chromatography.

Efficiency of separation depends on a number of factors: the nature of the eluant, pH of the medium, concentration of cations to be separated, nature of the ion-exchange resin, etc. A few papers have been published relating to the development of methods for the chromatographic separation of ultra-small amounts of rare earth elements using various eluants. Kettelle and Boyd succeeded, in the course of 30 hours, in separating traces of elements of the yttrium group by washing with ammonium citrate [1]. More recently ammonium lactate has been used [2-4]. Mayer and Freiling [5], who carried out separations of the pairs Sm – Eu, and Eu – Tb, with solutions of lactates, glycolates, citrates, etc., found that lactates are the best eluants. Rapid separation of elements of the cerium group on Zeokarb resin, by washing with ammonium lactate [6], was achieved in 1955

It is known [1], that separation of elements of the yttrium group is more difficult than separation of cerium group elements. The methods described in the literature for separating yttrium group elements have the one big drawback that separation takes too long.

The work described here, had as its aim, development of a rapid and efficient chromatographic separation of the radio-isotopes of the heavy rare earths obtained during fission of ytterbium and hafnium by high energy protons. In order to find the optimum conditions for such a separation, we studied the effect of the following factors on the efficiency of separation: a) the nature of the eluant (ammonium oxalate and ammonium lactate); b) pH of the ammonium lactate solution; c) the amount of carrier.

METHOD

70-80 mg of ytterbium acetate or hafnium hydroxide were irradiated by 660 mev protons on the USSR Academy of Sciences Institute of Nuclear Problems synchrotron. Irradiated preparations were dissolved in 5% acetic acid and a mixture of 0.5 N HCl and 5% oxalic acid, respectively. In view of the fact that such amounts of bombarded elements may have a strong effect on the efficiency of separation of the rare earth elements [7], it is necessary to split the basic mass of ytterbium and hafnium.

Electrolysis with a mercury cathode which is a method developed by coworkers in the Geochem. Inst. of the USSR Academy of Sciences was used for separating ytterbium. The conditions used for electrolysis were as follows: the pH of the ytterbium acetate and potassium citrate solution, which was added for preventing precipitation of ytterbium, was 5-6; current density – 0.05 a/cm^2; D. C. voltage 12 volts; temperature of solution 0-5°; duration of electrolysis ~ 1 hour. A special apparatus (Fig. 1) was made for the electrolytic deposition of ytterbium and its subsequent separation from mercury. Electrolysis was conducted in vessel 1; on termination of the electrolysis, by opening tap 3, the mercury passed into vessel 4, which contained water. Here the ytterbium amalgam was washed free of impurities; it was then transferred into vessel 6 by means of hot dilute HCl (1 : 1), where the ytterbium amalgam was decomposed. The solution from the electrolyzer was transferred into vessel 4 and collected via outlet 7 in a beaker. The yield of ytterbium in the amalgam was found experimentally to amount to 80-90%; ~ 2-4 mg of ytterbium remained in the solution together with the radio-isotopes of the rare earths. After evaporation of this solution and calcining the residue, the latter was dissolved in 2N HCl on heating; the insoluble residue was filtered off and ytterbium hydroxide precipitated from the filtrate with the radioisotopes of the rare earths by means of ammonia. The precipitate was removed from the solution by centrifuging, washed with distilled water and dissolved in 2-3 ml of 0.1 N HCl; adsorption of the rare earth elements from the solution was carried out in the course of 10-15 minutes by mixing the solution with a small amount of ion-exchange resin (~ 1/30 th of the amount of resin on the column). Adsorption amounted to 70-80%. The resin was then removed from the solution, washed with distilled water to remove acid, dried, and sprinkled into the column. Such a method of transferring the radio-isotopes on the resin, as a consequence of the formation of a narrow adsorption band in the column, has considerable advantages over the method normally used in the technique of chromatographic analysis [1, 7, 8].

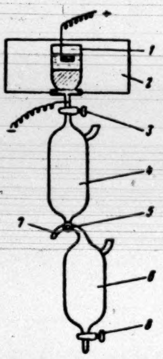


Fig. 1. Apparatus for electrolytic separation of ytterbium: 1) electrolyzer; 2) bath for cooling mixture; 3), 8) taps; 4) vessel for washing the ytterbium amalgam; 5) two-way tap; 6) vessel for decomposing the amalgam; 7) outlet for solution.

Separation of the radio-isotopes of the rare earths from bombarded hafnium was carried out by converting the latter into a complex with oxalic acid, with subsequent adsorption of the rare earths from 3-5 ml of solution with a small amount of resin in the H-form. It was shown experimentally that hafnium is not adsorbed under these conditions.

For chromatographic separation of the radio-isotopes of the rare earths a chromatographic column 25 cm long and 2 mm in diameter was used. Since high temperature favors more rapid separation [1], the column was provided with a sleeve in which water heated to 90° was circulated. In our experiments we used Dowex 50x−12 in the ammonium form; the resin particles were 250-400 mesh. The cation-exchange resin was heated in a small volume of water to remove air from it; it was then loaded into the column, which was filled with hot water; 2-3 ml of solution was passed through the column in order to establish a pH the same as that of the wash liquor in the column. The resin plus the radio-isotopes of the rare earths adsorbed on it was then loaded into the column.

The eluants used were 0.1% and 0.2% solutions of ammonium oxalate, and 0.4 M lactic acid of Russian make, purified on activated charcoal. Solutions of the latter were adjusted with concentrated ammonia solution to the required pH, which was measured on a tube pH meter, type LP-5 with a glass electrode.

In order to study the effect of different factors on separation efficiency, radioactive radio-isotopes of the rare earths: Lu^{177}, Yb^{175}, Tu^{170}, Er^{171}, Ho^{166}, obtained by bombarding the corresponding spectrographically pure oxides with slow neutrons, were used as well as radio-isotopes obtained during fission of ytterbium and hafnium by 660 mev energy protons. The radioactive purity of the radio-isotopes was determined by measuring their half-life periods, and the energy of their β-radiation, by absorption in aluminum. Radioactivity was measured on a TM-20 torsion counter with a Type B counting set-up. The half-life periods and the energy of these radio-isotopes showed good agreement with published results [9], as can be seen from the table.

During chromatographic separation of the elements each drop of the wash solution, 0.04-0.05 ml, was collected on 35 x 25 mm sheets of tracing paper, the solution evaporated, and their activity measured on a torsion counter.

TABLE

Elements	Radio-iso-topes	Half-life periods		E of β -radiation in Mev	
		found	published results	found	published results
Lu	Lu^{177}	6.5 days	6.8 days	0.45	0.46
Yb	Yb^{175}	105 hrs	102 hrs	0.43	0.45
Tu	Tu^{170}	—	—	0.85	0.9
Er	Er^{171}	—	—	1.6	1.6
Ho	Ho^{166}	28 hrs	30 hrs	1.7	1.6

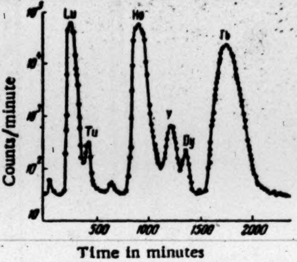


Fig. 2. Separation of mixtures of heavy rare earths by eluting with a 5% solution of ammonium citrate at a pH of 3.2

RESULTS

The most widely used eluants for separating the rare earths are solutions of ammonium citrate of varying pH [1, 7, 8, 10]. Nevertheless, in the case of heavy rare earths, efficient separation is not achieved when such an eluant is used, as can be seen e. g. from Fig. 2 [1]. In addition, the time taken to effect separation is very long (> 30 hours); accordingly, this method is not applicable for the separation of short lived isotopes. In this connection therefore, we attempted to use solutions of ammonium oxalate and lactate respectively for separating heavy rare earths.

1. Investigation of the Effect of the Nature of the Eluant

a) Elution with ammonium oxalate solutions. Fig. 3 illustrates the chromatogram obtained for a mixture of rare earths of the yttrium group when elution was carried out with 0.1% and 0.3% ammonium oxalate solutions. It is clear from this chromatogram that separation efficiency is not high: lutecium and ytterbium are poorly separated, while thullium and erbium, holmium and dysprosium are eluted together. Another vital drawback is the time of separation: in our tests, elution took 30 hours. Consequently, the use of ammonium oxalate solutions did not give the desired results; we, accordingly, concentrated on the use of ammonium lactate.

b) Elution with ammonium lactate solutions. As noted already the pH of the eluant is of great importance in the separation of the rare earths. It is essential to find that value of the pH at which it would be possible to use those small differences in the stability of their complexes, which would guarantee efficient separation of the rare earths. On Figs. 4, 5, 6, 7, and 8 are shown chromatograms reflecting the effect of the pH of the ammonium lactate solution on separation efficiency; in two experiments (Figs. 4 and 5), 0.01 mg of the rare earth element was used in each case.

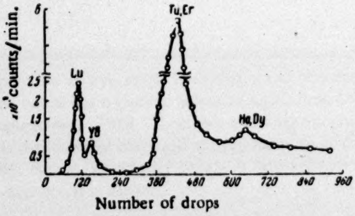


Fig. 3. Separation of a mixture of rare earths of the yttrium group (0.01 mg in each case), bombarded by slow neutrons, by eluting with 0.1 and 0.3% ammonium oxalate solutions. Up to 600 drops – 0.1% solution; subsequently –0.3%; rate 0.04 ml/minute.

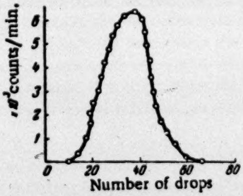


Fig. 4. Separation of Lu, Yb, Tu (0.01 mg of each) with ammonium lactate at a pH of 4.2; rate 0.04 ml/minute; t 90°.

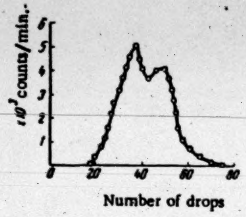


Fig. 5. Separation of Lu, Yb, Tu (0.01 mg of each) with ammonium lactate at a pH of 4.0; rate 0.04 ml/minute; t 90°.

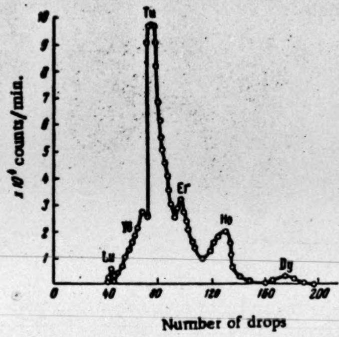


Fig. 6. Separation of radio-isotopes of elements of the yttrium group, obtained by fussion of ytterbium with 660 mev protons, with ammonium lactate at a pH of 3.65; rate 0.04 ml/minute; t 90°.

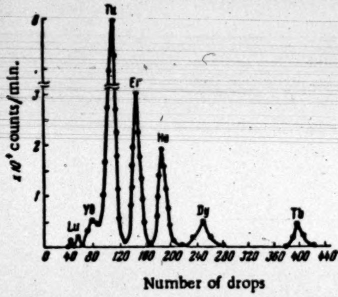


Fig. 7. Separation of radio-isotopes of elements of the yttrium group, obtained during fission of ytterbium by 660 mev protons, at a pH of 3.4. Starting at 300 drops at pH 3.65; rate 0.04 ml per minute; t 90°.

Examination of the chromatograms shown on these figures show the considerable effect which eluant pH has on separation efficiency. Separation is most efficient at a pH of 3.4 (Figs. 7, 8). At high pH values either separation is inefficient or no separation occurs at all. We also carried out experiments with solutions having pH < 3.4; they showed that under these conditions separation takes a considerable time (15-20 hours); in addition, the peaks obtained are drawn out.

Comparison of results of separation of heavy rare earths by various eluants: ammonium citrate, ammonium oxalate, and ammonium lactate (Figs. 2, 3, and 7), show that the most efficient separation is achieved when ammonium lactate at a pH of 3.4 is used as eluant. Elution of yttrium group rare earths takes 3-6 hours.

2. Study of the Effect of the Amount of the Carrier

It is pointed out in the literature [7], that if separation of rare earths is carried out at concentrations greater than trace amounts, the concentrations of the rare earths has a marked effect on separation. Lavrukhina [11] observed an appreciable increase in the rate of displacement of the Y^{91} component along the chromatographic column on decreasing its content rapidly. Since this phenomenon may lead to accumulation of the bands of two or more elements, if their amounts differ considerably, then it is necessary to take it into account during chromatographic separation of mixtures, in the presence or absence of a carrier.

In our experiments, 2-4 mg of ytterbium was left with the micro-amounts of other elements after electrolytic deposition of the ytterbium. Accordingly, we studied the effect of different concentrations of ytterbium on the efficiency of its separation from thullium. The experimental results are shown on Fig. 9 (a, b, c). It is clear from these results how the amount of ytterbium affects the efficiency of its separation from thullium; at

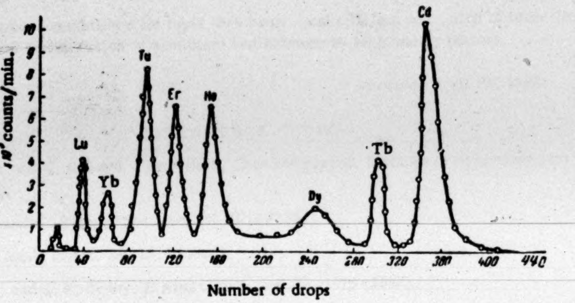


Fig. 8. Separation of radio-isotopes of elements of the yttrium group, obtained during fission of hafnium by 660 mev protons, by means of ammonium lactate at a pH of 3.4; rate 0.04 ml/minute; t 90°; starting with 290 drops at a pH of 3.65.

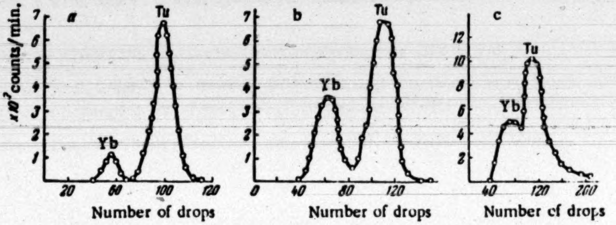


Fig. 9. Separation of Yb and Tu by ammonium lactate at various concentrations ratios of these elements; pH 3.4; rate 0.04 ml/minute; t 90°; a) Tu – 0.01 mg; Yb – 0.01 mg; b) Tu – 0.01 mg; Yb – 0.1 mg; c) Tu – 0.01 mg; Yb – 1.5 mg.

concentration ratios of these elements to each other of 150 : 1 no separation is observed. As a result we were unable to separate thullium and ytterbium from the products of the bombardment of the latter by high energy protons (Fig. 10).

In conclusion I wish to thank A. K. Lavrukhina for useful advice in carrying out the work described here.

SUMMARY

1. The effect of the nature of the eluant (ammonium oxalate, ammonium lactate) on the separation efficiency of yttrium group elements has been studied. Best results were obtained on using a 0.4 M ammonium lactate solution at a pH of 3.4 as eluant; the use of solutions whose pH > 3.4, leads to inefficient separation, while lower pH values means that elution takes a long time.

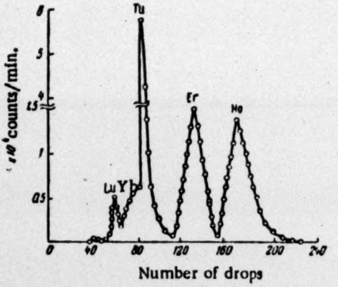


Fig. 10. Separation of radioisotopes of elements of the yttrium group, obtained during fission of ytterbium with 660 mev protons, by ammonium lactate; pH 3.4; rate 0.04 ml/minute; t 90°.

2. The amount of carrier (> 0.1 mg) affects separation efficiency of a given element from its neighbors; separation deteriorates significantly.

3. Conditions have been established for rapid (3-6 hours), and efficient separation of radio-isotopes of the yttrium group, obtained during fission of ytterbium and hafnium by high energy protons.

Received April 23, 1956.

LITERATURE CITED

[1] V. Kh. Kettele and G. E. Boyd, Symposium, Chromatographic Methods of Separating Ions (Foreign Lit. Press, Moscow, 1949).

[2] H. G. Petrow, and G. Rocco, Phys. Rev. 96, 1614 (1954).

[3] H. G. Petrow, Anal. Chem. 26, 1514 (1954).

[4] E. C. Freiling, and L. K. Bunny, J. Am. Chem. Soc. 76, 1021 (1954).

[5] S. W. Mayer, and E. C. Freiling, J. Am. Chem. Soc. 75, 5647 (1953).

[6] G. Cuningnamel, and M. L. Sizeland, J. Inorg. Nuclear. Chem. 1, 163 (1955).

[7] E. R. Tomkins and S. W. Mayer, Symposium, Chromatographic Methods of Separating Ions (Foreign Lit. Press, Moscow, 1949).

[8] E. R. Tomkins, I. Kim, and V. E. Kon, Symposium, Chromatographic Methods of Separating Ions (Foreign Lit. Press, Moscow, 1949).

[9] I. P. Selinov, The Atomic Nucleus and Nuclear Transformations (1951), Vol. 1.

[10] F. Kh. Spedding, A. F. Voigt, E. M. Gledroy, N. P. Sleit, and I. E. Powell et al, Symposium, Chromatographic Methods of Separating Ions (Foreign Lit. Press, Moscow, 1949).

[11] A. K. Lavrukhin, Doctor's Thesis (Geochem. Inst. Acad. Sci. USSR, Moscow, 1955).

VANADOMETRIC DETERMINATION OF 5, 7-DIBROMOHYDROXYQUINOLINE AND DIBROMOHYDROXYQUINOLATES

V. A. Nazarenko and S. Ya. Vinkovetskaya

5, 7-Dibromo-8-hydroxyquinoline (5, 7-dibromo-oxine) is superior in many respects to 8-hydroxyquinoline and allows separation, in some cases, of metals with similar analytical properties, which cannot be separated by means of 8-hydroxyquinoline. In particular, by means of dibromohydroxyquinoline, it is easy to separate gallium from fairly large amounts of alluminum [1].

Dibromohydroxyquinoline finds its chief application for gravimetric determinations of metals; spectrophotometric determination of galliumby means of dibromohydroxyquinoline [2], is not very convincing. Gravimetric determination of gallium [1], copper, iron, and titanium [3], aluminum [4], lead [5], vanadium [6], and germanium [7], as dibromohydroxyquinolates, has been described. Volumetric methods of determining metals precipitated as their dibromohydroxyquinolates are not known becasue of absence of a reliable volumetric method of determining dibromohydroxyquinoline. The bromatometric method which is widely used for determining 8-hydroxyquinoline and 8-hydroxyquinolinates, is inapplicable to dibromohydroxyquinoline which is the end product of the bromination of 8-hydroxyquinoline in aqueous solutions. A method which has been suggested for determining bioform (5-chloro-7-iodohydroxyquinoline), and vulnaline (5-chloro-7-bromohydroxyquinoline) in pharmaceutical products and in dressing materials, and which is based on argentometric titration of the halogen split off by nitric acid [8], is not very accurate, and has not found application for determining metal 5, 7-dibromohydroxyquinolates. In the search for a volumetric method of determining dibromohydroxyquinoline, which is also suitable for determining dibromohydroxyquinolates, we turned to the vanadometric method developed by Syrokomsky and coworkers [9], which is already being used for the analysis of organic materials both by Syrokomsky himself, and also by other investigators [10]. During oxidation of organic matter in sulfuric acid, quinquevalent vanadium is reduced to the quadrivalent state. When correctly chosen conditions are used there is a stoichiometric relation between vanadate and organic material. The aim of the work described here was to find such relation for dibromohydroxyquinoline.

Determination of 5, 7-Dibromohydroxyquinoline

1. 5, 7-Dibromohydroxyquinoline. The marketed product was crystallized three times from benzene and then dried at 105°. A 0.01 M solution was prepared in 10 N sulfuric acid (3.0297 mg/ml).

2. Copper dibromohydroxyquinolate was prepared by precipitating copper with recrystallized dibromohydroxyquinoline under conditions recommended for its gravimetric determination. Two solutions were prepared:

a) 43.2 mg of the dibromohydroxyquinolate, dried at 140°, was dissolved in 50 ml 10 N sulfuric acid;

b) 188.2 mg of the dibromohydroxyquinolate was dissolved in 100 ml 10 N sulfuric acid.

3. Ammonium metavanadate (analytical grade) was twice recrystallized from weak ammonia solution. 0.02 and 0.05 N solutions respectively were prepared in 6N sulfuric acid. These solutions were standardized by titrating with 0.02 or 0.05 solutions respectively of Mohr's salt in 6 N sulfuric acid in the presence of phenylanthranilic acid. The Mohr's solutions were standardized in their turn with potassium dichromate, also in the presence of phenylanthranilic acid.

On varying the oxidation conditions of dihydroxyquinoline by vanadate, constant and reproducible results were obtained under the following conditions. To a measured volume of dibromohydroxyquinoline or copper dibromohydroxyquinolate solution was added up to 75 ml of 10 N sulfuric acid; this was followed by 25-50 ml of 0.05 N vanadate solution. The amount of dibromohydroxyquinoline should be such that after oxidation, an excess of vanadate not less than 5-6 ml should remain. The mixture was heated to the boil and boiled for 1 minute, after which it was kept on a boiling water bath for 1 hour. The mixture was cooled and excess vanadate titrated with 0.05 N Mohr's salt using phenylanthranilic acid as indicator.

TABLE 1

Titration of Dibromohydroxyquinoline

Dibromohydroxyquinoline taken in mg	0.5 N NH_4VO_3 used in ml	g-equiv. of dibromohydroxyquinoline	Dibromohydroxyquinoline found in mg	Difference in mg
3.030	1.95	31.074	2.944	—0,086
3.030	2.05	29.759	3.105	+0.075
3.030	2.00	30.297	3.030	0
9.089	6.13	29.587	9.286	+0.197
9.089	6.03	30.146	9.134	+0.045
12.119	7.83	30.955	11.861	—0.258
12.119	8.06	30.073	12.208	+0.089
12.119	7.96	30.449	12.058	—0.061
18.178	11.89	30.577	18.012	—0.166
18.178	12.02	30.246	18,208	+0.030
30.297	19.77	30.649	29.949	—0.348
30.297	19.86	30,510	30.085	—0.212
Mean		30.343		
Theoretical		30.297		

Experimental results are given in Tables 1 and 2, which also include the gram-equivalents of dibromohydroxyquinoline and copper respectively calculated from them. The experimentally determined gram-equivalent of dibromohydroxyquinoline was found to be very near to 30.297, which is the figure obtained on dividing the molecular weight of dibromohydroxyquinoline (302.97) by 10. The experimentally determined gram-equivalent of copper was found to be 3.177 which is the figure obtained on dividing the atomic weight of copper (63.54) by 20; this corresponds to the formula $Cu(C_9H_4ONBr_2)_2$.

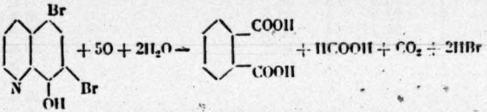
TABLE 2

Titration of Copper Dibromohydroxyquinolate

Cu dibromohydroxyquinolate taken in mg	0.05 N NH_4VO_3 used in ml	Gram-equiv. of dibromohydroxyquinoline	Gram-equiv. of Cu
4,32	2.55	30.758	3.225
5.20	3.16	29.877	3.133
8.64	5,30	29.597	3.104
8.64	5.20	30.167	3.163
10,40	6.22	30.357	3.183
17,28	10.40	30.167	3.163
20.80	12.24	30.853	3.235
41.60	24.88	30.357	3.183
Mean		30.267	3.172
Theoretical		30.297	3.177

Accordingly, 10 gram-equivalents of vanadate are used for the oxidation of one mole of dibromohydroxyquinoline. Table 1 also contains the values for the amounts of dibromohydroxyquinoline found by titration, and calculated on the basis of the theoretical gram-equivalent (30.297). From these results it is clear that experimental error is less than ± 3%.

In work devoted to vanadometric determination of organic substances [9 (Chapter V), 10], the gram-equivalent of the organic material has been determined empirically without investigating the chemistry of the oxidation reaction. We managed to establish that during oxidation of dibromohydroxyquinoline by vanadate under the conditions described above, the dibromohydroxyquinoline is oxidized to pyridine-2, 3-dicarboxylic (quinolinic) acid with simultaneous formation of formic acid, carbon cioxide, and hydrogen bromide. The reaction follows the equation:



This part of the work will be described in detail elsewhere.

Application of the Method for Volumetric Determination of Metals

Metal dibromohydroxyquinolates dissolve readily in 10 N sulfuric acid, in which dibromohydroxyquinoline can be determined afterwards by the method described above. The gram-equivalent of the metal should be calculated from the ratio A/10n, where A is the atomic weight of the metal, while n is the number of dibromohydroxyquinoline residues combined with the metal in the molecule of the dibromohydroxyquinolate. Since n is usually 2, 3, and even 4, the gram-equivalents obtained are very small, which means that it is possible to determine milli- and submilli-gram amounts of metals macrochemically.

We have determined copper, iron, gallium, titanium, and molybdenum after their precipitation by dibromohydroxyquinoline according to published procedures. In addition, we have studied the possibility of carrying out vanadometric determinations of germanium and silicon, after precipitation of germanomolybdic and silicomolybdic acids respectively, with dibromohydroxyquinoline.

It should be noted that the method is only applicable to the determination of those metals which are precipitated quantitatively by dibromohydroxyquinoline in acid solution (pH < 3) since at higher pH, the dibromohydroxyquinolate precipitate is contaminated by free dibromohydroxyquinoline as a result of the hydrolysis of the salts of 5, 7-dibromo-8-hydroxyquinoline. Thus, we were unable to apply this method to aluminum, lead, and vanadium.

During gravimetric determination of these metals by means of dibromohydroxyquinoline [4-6] the precipitates are dried at 190-200°, at which temperature free dibromo-oxine, which may have been coprecipitate, is volatile. The vanadometric method can therefore still be applied to such metals as aluminum, lead and vanadium, if the precipitates of their dibromohydroxyquinolates, before dissolving in sulfuric acid, are kept for long enough at 190-200°. This operation however, complicates and lengthens the method.

Experimental Procedure. The test element is precipitated with dibromohydroxyquinoline, and the precipitate filtered through a wad of asbestos placed in a funnel. The asbestos wad is first freed from iron by boiling it with hydrochloric acid. Filter plus precipitate and the vessel in which precipitation has been effected, are washed with wash liquor, and then three times with water. Washed precipitate and filter are then washed into the vessel in which precipitation has been effected, using 75 ml of 10 N sulfuric acid, and the mixture is heated till the dibromohydroxyquinolate dissolves. Vanadate solution is then added and the procedure described already followed.

Solutions of test elements were prepared from preparations of established purity.

The content of an element in solution was determined gravimetrically.

Copper. Precipitation of $Cu(C_6H_4ONBr_2)_2$ was carried out by means of the procedure described in [3]. Gram-equivalent 63.54/20 = 3.177.

Results are given in Table 3.

TABLE 3

Determination of Copper

Cu taken in mg	Cu found in mg	Difference in mg
0.41	0.41	0
0.49	0.50	+0.01
0.82	0.84	+0.02
0.82	0.83	+0.01
0.99	0.99	0
1.64	1.65	+0.01
3.96	3.95	—0.01

TABLE 4

Determination of Iron

Fe taken in mg	Fe found in mg	Difference in mg
0.52	0.54	+0.02
1.04	1.02	—0.02
1.55	1.49	—0.06
2.07	2.00	—0.07

Iron. Precipitation of $Fe(C_9H_4ONBr_2)_3$ was carried out according to [3].

Gram-equivalent 55.85/30 = 1.8617.

Results are given in Table 4.

Gallium. Precipitation of gallium was carried out by the method described in [1] plus some modifications. To 100 ml of gallium solution containing 4 ml of 6 N hydrochloric acid, is added 20 ml acetone, the mixture heated to the boil and 15-25 ml of 0.3% dibromo-oxine in acetone added. The whole is carefully boiled for 15 minutes, and then heated on a water bath for 1 hour. It is filtered while hot, and the precipitate washed with a hot 20% solution of acetone in 0.05 N hydrochloric acid, and finally washed with water.

Formula of the precipitate $Ga(C_9H_4ONBr_2)_3$.

Gram-equivalent 69.72/30 = 2.324.

Results are given in Table 5.

TABLE 5

Determination of Gallium

Ga taken in mg	Ga found in mg	Difference in mg	Ga taken in mg	Ga found in mg	Difference in mg
0.20	0.22	+0.02	1.00	0.99	—0.01
0.50	0.51	+0.01	1.20	1.20	0
0.50	0.49	—0.01	1.86	1.84	—0.02
0.50	0.50	0	4.00	4.05	+0.05
1.00	1.01	+0.01	4.65	4.70	+0.05

Titanium. Precipitation of $TiO(C_9H_4ONBr_2)_2$ was carried out according to [3].

Gram-equivalent 47.90/20 = 2.395.

Results are given in Table 6.

Molybdenum. The following conditions were developed in order to precipitate molybdenum as the dibromohydroxyquinolate $Mo_2O_2(C_9H_4OHBr_2)_2$, free from coprecipitated dibromohydroxyquinoline. To 10 ml of molybdate solution, 0.1 N with respect to hydrochloric acid, is added, in the cold, 10 ml of acetone, and, after mixing, 5 ml of 0.6% solution of dibromohydroxyquinoline in hydrochloric acid (1:1). The mixture is left for 30 minutes, filtered and then washed with cold 15% solution of acetone in 0.05 N hydrochloric acid, followed by cold water. The precipitate is then dissolved in 10 N sulfuric acid and the procedure described already followed.

Gram-equivalent 95.95/20 = 4.7975.

Results are given in Table 7.

TABLE 6

Determination of Titanium

Ti taken in mg	Ti found in mg	Difference in mg
0.13	0.14	+0.01
0.13	0.13	0
0.62	0.59	−0.03
1.25	1.20	−0.05

TABLE 7

Determination of Molybdenum

Mo taken in mg	Mo found in mg	Difference in mg
0.30	0.30	0
0.50	0.50	0
0.60	0.60	0
1.00	1.01	+0.01
1.50	1.48	−0.02
2.00	2.01	+0.01

Germanium. Dibromohydroxyquinoline does not precipitate germanium; in acid solution however, it precipitates germanomolybdic acid, and this reaction has been used for gravimetric determination of germanium [7, 11]. For volumetric determination of germanium, formation of germanomolybdic acid, and precipitation of the latter by dibromohydroxyquinoline were carried out according to [7].

Formula of precipitate [11]:

$$(C_9H_4ONBr_2)_4 \cdot H_4[Ge(Mo_{12}O_{40})] \cdot H_2O$$

Gram-equivalent 72.60/40 = 1.815.

Results are given in Table 8.

TABLE 8

Determination of Germanium

Ge taken in mg	Ge found in mg	Difference in mg
0.20	0.21	+0.01
0.50	0.47	−0.03
0.70	0.69	−0.01
1.00	0.98	−0.02
2.00	2.05	+0.05

TABLE 9

Determination of Silicon

Si taken in mg	Si found in mg	Difference in mg
0.20	0.21	+0.01
0.40	0.406	+0.006
0.50	0.51	+0.01
0.70	0.70	0
1.00	0.98	−0.02

Silicon. In its analytical properties silicomolybdic acid resembles germanomolybdic acid very closely. We suggest therefore that it should be possible to determine silicon under the same conditions as those used for determining germanium. To 2 ml of a very weak alkaline solution of sodium silicate is added 3 ml of 5% ammonium molybdate and 1 ml 2 N sulfuric acid. After 10 minutes this solution is diluted with water to 10 ml; 5 ml of concentrated hydrochloric acid is then added, followed by 5 ml of a 0.6% solution of dibromohydroxyquinoline in hydrochloric acid (1:1), added dropwise with stirring. The precipitate is filtered and washed 4 times with wash liquor (10 ml water, 10 ml concentrated hydrochloric acid and 1 ml reagent), and then 3 times with water. The precipitate is finally dissolved in 10 N sulfuric acid and the procedure described above then followed.

The formula of the silicomolybdate of dibromo-oxine can, by analogy with that of the germanomolybdate be written as follows:

$$(C_9H_4ONBr_2)_4 \cdot H_4[Si(Mo_{12}O_{40})] \cdot nH_2O.$$

Gram-equivalent 28.06/40 = 0.7015.

Results are given in Table 9.

As can be seen from the results given above, the vanadometric method permits one to determine both dibromohydroxyquinoline as well as individual elements which are precipitated by dibromohydroxyquinoline in acid solution. Thanks to the low value of the gram-equivalents, it is possible by means of the vanadometric method to determine milli- and submilli-gram amounts of elements with satisfactory accuracy.

SUMMARY

Conditions have been found for carrying out vanadometric determination of 5, 7-dibromohydroxyquinoline, and the chemistry of the oxidation of dibromohydroxyquinoline by vanadate has been clarified. The gram-equivalent of the dibromo-oxine is equal to Molecular Weight/10.

It has been shown that it is possible to carry out vanadometric determination of metals precipitated by dibromohydroxyquinoline in acid solution (pH < 3), and also of elements which form heteropoly acids. The method has been illustrated by reference to the determination of copper, iron, gallium, titanium, molybdenum, germanium, and silicon.

Received January 26, 1956.

LITERATURE CITED

[1] E. Gastinger, Z. anal. Chem. 126, 373 (1943).

[2] T. Moeller, and A. J. Cohen, Anal. Chim. Acta 4, 316 (1950).

[3] R. Berg, and H. Küstenmacher, Z. anorg. u. allgem. Chem. 204, 215 (1932).

[4] A. Zanko and A. Bursuk, J. Appl. Chem. 9, 895 (1936).

[5] A. Zanko and A. Bursuk, J. Appl. Chem. 9, 2297 (1936).

[6] I. P. Alimarin and V. G. Kryukov, J. Anal. Chem. 10, 56 (1955) (T. p. 49).*

[7] G. Bartelmus, and F. Hecht, Mikrochim. Acta 1, 148 (1954).

[8] H. Wojahn, Pharm. Zentralhalle 85, 15 (1947).

[9] V. S. Syrokomsky and Yu. V. Klimenko, Vanadometry (Metallurgy Press, Sverdlovsk, 1950).

[10] Z. P. Suranova, Trans. Odessa University, Chem. Faculty 3, 73 (1953).

[11] T. Dupuis, Mikrochemie ver. Microchim. Acta, 35, 449 (1950).

---

*T. p. = C. B. Translation pagination.

CATION-EXCHANGE PROPERTIES OF PHENOL-FORMALDEHYDE RESINS IN RELATION TO THE TYPE OF ACID GROUP

E. B. Trostyanskaya, I. P. Losev, and A. S. Tevlina

The D. I. Mendeleev Chemico-Technological Institute

The ever increasing application of cation-exchange processes for separating complex mixtures has been the result of successes achieved in the separation of the alkali, rare earth, and other elements, and of complex mixtures of amino acids, amines, etc. [1-5].

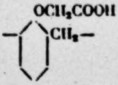
Analysis of the results obtained leads one to conclude that the solution of any one particular problem of separation requires careful selection of the requisite conditions. Using one ion-exchange resin, it is possible, by changing sorption conditions (rate of filtration, sorption temperature, particle size of the resin, and column size) [6], or choosing a selectively acting displacer (eluant) [7], to separate different ions. Nevertheless, varying only the soprtion conditions, does not, in all cases, lead to the required results, and changing the structure of the sorbent itself is oftern more effective. Numerous tests indicate, e. g. that it is possible to change the rate at which ion-exchange equilibrium is reached, and to alter the capacity of the ion-exchange resin with respect to different ions, by varying the degree of swelling of the resin [8, 10]. Even greater possibilities of successful application of ion-exchange processes in chromatographic analysis are opened up by the production of cation-exchange sorbents which differ from each other with respect to the acid groups they contain [11-13]. Ion-exchange sorption is based on a chemical reaction which takes place between sorbent (acid) and a solution of a salt. Naturally, the result of an ion-exchange process will, above all, be determined by the type of acid group in the resin, and by the nature of the cations. Accordingly, ion-exchange resins which can be used for various problems in analytical chemistry must be regarded as a totality of characteristic reagents, each of which is only suitable for a certain number of investigations. Only a collection of similar ion-exchange resins whose properties are known in detail can, in the hands of the analyst, serve as a basis for a new, simple, and often unique method, of separating mixtures [14, 15].

Modified phenol-formaldehyde resins [16, 17], have found wide use in the production of cation-exchange resins.

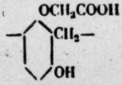
Phenol-formaldehyde resins are weak acids as a result of the fact that, as a rule, the hydroxyl groups of the phenols do not enter into the resin forming reaction and preserve the properties inherent in the original phenol. Thus, in resorcinol-formaldehyde resin (Resin "R") acid properties should be more clearly manifest than in a phenol-formaldehyde resin (Resin "Ph"). The results of potentiometric titrations of Resin "R" and Resin "Ph" which are given in Fig. 1 confirm these conclusions (potentiometric titration of the cation-exchange resins was carried out by a method described in the work of Kunin and Meyer [18]).

The high reactivity of phenol-formaldehyde resins permits them to be used as "acid-holders" for various types of acid groups. In this case, the structure of the resin skeleton remains unchanged, thereby enabling one to study the effect of only the acid groups on the cation-exchange properties of the resin.

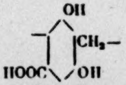
By introducing carboxyl groups into a phenol-formaldehyde resin it is possible to change the degree of dissociation of these insoluble high molecular weight acids, and consequently, their behavior in ion-exchange processes. The carboxyl group can occupy a different position in the elementary cell of the resin macro-molecule. Resins the structure of the elementary cell of which can be represented as follows, were studied:



Resin "CPh"



Resin "CR"



Resin Wofatite S

As can be seen from the formula adduced above, the carboxyl group which may be in the side chain or may be directly connected with the benzene ring, may be the sole acid group, or may be present at the same time as hydroxyl groups. The effect of the hydroxyl groups and of the position of the carboxyl group in the structure of the elementary cell of the resin, on the extent to which acid properties are manifested, can be established on the basis of results of potentiometric titration (Fig. 2). Comparison of these results show that connecting the carboxyl group directly to the benzene ring leads to an increase in the acid properties of the resin. The latter also become stronger with increasing number of hydroxyl groups in the elementary cell. For the sake of comparison, on the same diagram are also given the results of titrating sorbent "CM" (a methacrylic acid polymer).

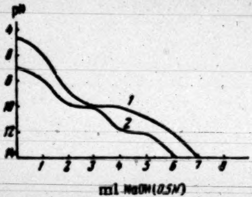


Fig. 1. 1) Resin "R" 2) Resin "Ph".

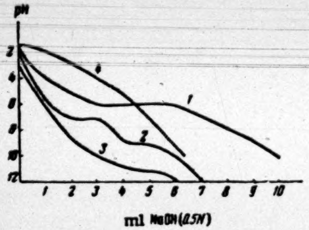


Fig. 2. 1) CM; 2) CR; 3) CPh; 4) Wofatite S.

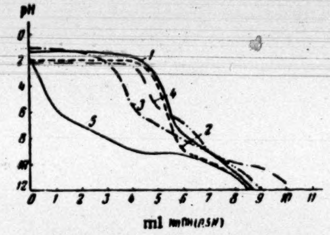
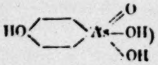
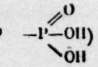
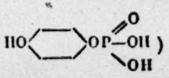
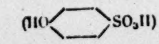
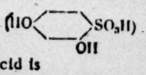
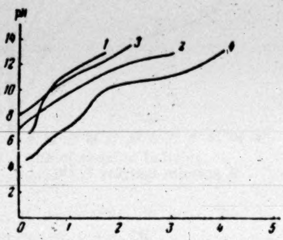


Fig. 3) 1) MSR; 2) MSPh 3) RPh−1; 4) RPh−2; 5) APh.

The acid properties of phenol-formaldehyde resins can be varied by introducing another type of acid group. Thus, we prepared insoluble high molecular weight hydroxyphenylarsonic acids (ionogenic group  Resin "APh"; insoluble monophenylphosphates (inonogenic group  Resin "RPh-2"; monohydroxyphenylphosphates (ionogenic group  Resin RPh-1";

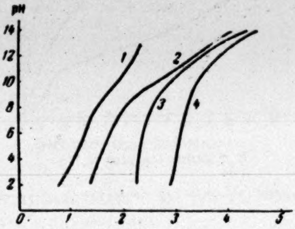
monophenylsulfonic acids  Resin"MSPh"; and dihydroxyphenylsulfonic acids  Resin "MSR". Results for the potentiometric titration of these resins (Fig. 3) show that the weakest acid is "APh"," which contains arsonic groups. The strongest acids are Resins "RPh-1", "MSR", and "MSPh".

Most of the ion-exchange phenol-formaldehyde resins prepared are insoluble acids with differing degrees of dissociation of their individual acid groups. This property should be reflected not only in the results of potentiometric titration, but also in the absorptive capacity of the sorbent determined at different values of the pH of the original solution. Results of these investigations are illustrated in Figs. 4 and 5. Experiments were carried out as follows: to approximately 1 g of regenerated and washed resin, particle size 0.1-0.25 mm, was added 50 ml of NaCl solution whose pH had been adjusted by addition of either NaOH or HCl. After keeping the samples for 24 hours at 18-20°, the resin was removed and the amount of sodium ions absorbed by it determined.



Capacity with respect to Na^+ in mg-equiv/g

Fig. 4. 1) "Ph"; 2) "R"; 3) "CPh"; 4) "CR".



Capacity with respect to Na^+ in mg-equiv/g

Fig. 5. 1) Resin "APh"; 2) Resin "RPh-2"; 3) Resin "MSPh"; 4) Resin "RPh-1".

The presence of two types of acid groups, which differ considerably with respect to their degree of dissociation, is clearly shown on the curves for Resins CR, RPh-2, and MSPh (Figs. 4 and 5). The first acid group enters into the ion-exchange reaction at a pH of 1-2; the second starts to combine at a pH of 8-9, giving a break. At the same time the absorptive capacity of sorbents containing weakly acid groups (Resins Ph, R, CPh, APh) increases smoothly with decreasing hydrogen ion concentration of the original solution.

Numerous studies of various ion-exchange resins have shown that the rate at which sorption equilibrium is established depends to a certain extent on the rate of diffusion of the cation inside the grain of sorbent [11, 12]. There is a basis however, for assuming that the degree of dissociation of acid groups should also affect the rate at which sorption equilibrium is established [19].

The group of cation-exchange resins which we studied have macro-molecules of similar structure; the swelling coefficient varies from 0.4-0.7 in neutral solutions; accordingly one can assume that the permeability of resin grains for the same cation should differ very little. Only Resins "Ph" and "R" whose macro-molecules have a less permeable structure and with a swelling amounting to 10%, are exceptions. On Figs. 6 and 7 are given results for the study of the rate at which sorption equilibrium is established; these confirm the assumption that the rate of ion-exchange reactions between resin and a solution of an electrolyte depends not only on the permeability of the resin, but also, to a significant extent, on the degree of dissociation of its acid groups. Studies were carried out under identical conditions, and at a pH of 9 for the original solution, which ensures an ion-exchange reaction in weakly acid groups. The results indicated an unusually regular and sudden increase in the rate of the ion-exchange process with increasing degree of dissociation of the acid groups located in the resin structure. Resins belonging to weakly acid materials attain half of their full capacity after 80 hours; those belonging to average acid strength materials after 5 hours, and resins belonging to the strong acid type after 10-20 minutes.

In previous communications [12, 20], we have pointed out that sulfonated phenol-formaldehyde ion-exchange resins reduce certain cations during the ion-exchange process. Observations showed that under static conditions, the reduction process involves both the cations in the resin and cations remaining in solution. In each cycle, reduction proceeds right up to a definite maximum, the magnitude of which gradually falls with increasing number of cycles. After each regeneration the resin again acquires the capacity for reduction, but the amount of cations reduced decreases both in the resin and in solution. There is some reason for supposing that reduction proceeds between solution and resin independently of ion exchange and is determined by the presence in it of readily oxidized groups. This assumption is confirmed by a study of the reducing properties of various ion-exchange resins which we synthesized (Figs. 8 and 9). Phenol-formaldehyde and resorcinol-formaldehyde resins

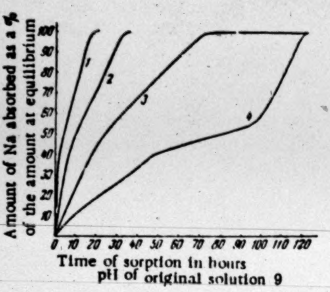


Fig. 6. 1) Resin "CR"; 2) Resin CPh" 3) Resin "R" 4) Resin "Ph".

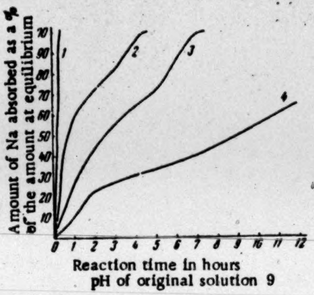


Fig. 7. 1) Resin "MSPh"; 2) "RPh-1"; 3) Resin "RPh-2"; 4) Resin "APh".

have aldehyde groups which lead to reduction reactions (Curves 1 and 2 in Fig. 8). Carboxyl groups do not lead to appreciable changes in the reducing properties of resins (Curves 3 and 4 in Fig. 8). Sulfonation and phosphorylation processes, obviously, are accompanied by partial oxidation of phenol groups in the resin; this explains the sharp increase in the reducing properties of resins in the first cycles of ion exchange. The extent of the reduction was determined under static conditions, by keeping 1 g of resin in 50 ml of 1.5% $FeCl_3$ for 24 hours and subsequently determining the amount of divalent ferrous ions both in solution and in the resin. Resins were regenerated with hydrochloric acid and further cycles were repeated under the same conditions.

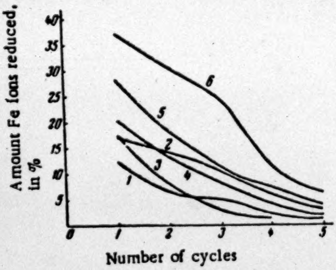


Fig. 8. 1) Resin "Ph"; 2) Resin "R"; 3) Resin "CPh"; 4) Resin CR; 5) Resin RPh-1; 6) Resin"MSPh".

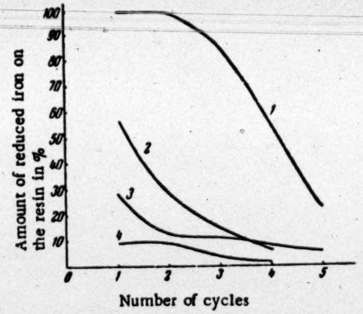


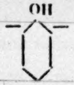
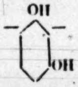
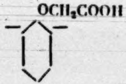
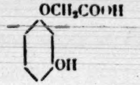
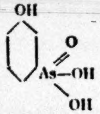
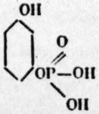
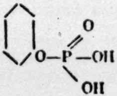
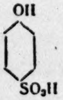
Fig. 9. 1) Resin MSPh; 2) Resin APh-1; 3) Resin RPh-1; 4) Resin RPh-2.

On Fig. 9 are shown the results of a study of the amount of reduced iron ions as a percentage of the total capacity of the given ion-exchange resin under static conditions; they show that sulfonated phenol-formaldehyde resins have the greatest reducing properties. The amount of readily oxidizable groups in the ion-exchange Resin "MSPh" is several times greater than the amount of ionogenic groups.

In conclusion we give in the table general characteristics of phenol-formaldehyde ion-exchange resins containing different acid groups.

TABLE

General Properties of Phenol-Formaldehyde Cation-Exchange Resins

Designation of the cation-exchange resin	Ionogenic group	Appearance of the resin	Swelling in %			acid No. in ml/g	capacity in terms of Ca in mg-equiv per g
			in water	in 5% HCl	in 0.5 N NaOH		
Phenol-formaldehyde Resin "Ph"		Amber colored, hard, brittle	10	0	56	174	—
Resorcinol-formaldehyde Resin "R"		Red, very hard	0	0	40	209	—
"CPh"		Red, brittle, readily ground	70	30	400	120	—
"CR"	 OCH₂COOH OH	Red, very stable	60	18	300	280	—
"APh"		Light gray, stable	50	20	85	190	1.8
"RPh 1"		Dark red, hard, very stable	40	25	200	260	4.2
"RPh 2"		Red, brittle	45	16	280	168	2.6
"MSPh"		Black, hard, brittle	70	30	120	330	2.5

SUMMARY

1. Ion-exchange processes which occur between high molecular weight, insoluble acids (cation-exchange resins) and the electrolyte of a solution, are determined by the nature of the acid groups, their mutual arrangement in the elementary cell of the resin macro-molecules, and by the structure of the "acid-holder".

2. A number of ion-exchange resins have been suggested which have "acid-holders" of identical structure, but with different acid groups arranged in different mutual positions in the elementary cell of the macro-molecules.

3. The presence in the ion-exchange resin of acid groups of varying degrees of dissocation is easily established by means of the "resin-capacity – pH of the original solution" curve.

4. It has been established that when the structure of the "acid-holder" is the same, the rate of the ion-exchange process increases with increasing degree of dissocation of the acid groups of the ion-exchange resin.

5. All the ion-exchange resins obtained by poly condensation of phenols and formaldehyde, apart from the type of acid groups, possess gradually decreasing reducing properties.

Received February 14, 1955.

LITERATURE CITED

[1] O. Samuelson, The Use of Ion Exchange in Analytical Chemistry (Foreign Lit. Press, Moscow, 1955).

[2] Trans. Comm. on Anal. Chem. (Acad. Sci. USSR Press, Moscow, 1955), Vol. VI.

[3] V. V. Rachinsky and T. B. Gapon, Chromatography in Biology (Acad. Sci. USSR Press, Moscow, 1953).

[4] Symposium, Chromatography (Acad. Sci. USSR Press, 1953).

[5] D. I. Ryabchikov and M. M. Senyavin, J. Anal. Chem. 8, 4, 195 (1953) (T. p. 215).*

[6] J. Schubert, Symposium, Ion Exchange (Foreign Lit. Press, Moscow, 1951), p. 175.

[7] D. I. Ryabchikov and E. A. Terenteva, Progr. Chem. 19, 220 (1950).

[8] K. W. Pepper, J. Appl. Chem. 1, 124 (1951).

[9] R. Kunin, and R. Myers, Disc. Faraday Soc. 7, 114 (1949).

[10] Tr. E. Kressman, and J. A. Kilcherer, J. Chem. Soc. 1949, No. 5, 1208.

[11] E. B. Trostyanskaya, Trans. Comm. on Anal. Chem. Vol. VI, p. 215 (1955).

[12] E. B. Trostyanskaya, I. P. Losev, and A. S. Tevlina, Progr. Chem. 24, No. 1, 71 (1955).

[13] R. Griessbach, Z. Elektrochem. 57, 3, 147 (1953).

[14] V. I. Kuznetsov, Trans. Comm. on Anal. Chem. Vol. VI, p. 249 (1953).

[15] R. Griessbach, Angew. Chem. 76, 583 (1955).

[16] I. P. Losev, E. B. Trostyanskaya, and A. S. Tevlina, J. Chem. Ind. 8, 8, (1950).

[17] I. P. Losev, E. B. Trostyanskaya and A. S. Tevlina, Trans. All-Union Conference on Chromatography, 21-24 November 1950, Moscow (Acad. Sci. USSR Press, 1952), p. 103.

[18] R. Kunin and R. Meyer, Ion Exchange Resins (Foreign Lit. Press, Moscow, 1952), p. 158.

[19] V. Bauman, Symposium, Ion Exchange (Foreign Lit. Press, Moscow, 1951), p. 66.

[20] I. P. Losev and A. S. Tevlina, Trans. Comm. on Anal. Chem. Vol. VI, p. 326 (1955).

---

*T. p. = C. B. Translation pagination.

COLORIMETRIC METHODS OF DETERMINING SMALL AMOUNTS OF THALLIUM

N. T. Voskresenskaya

M. V. Lomonosov Moscow State University

Recently, both here and abroad, a large number of articles have appeared which have been devoted to methods for determining small amounts of thallium; these include several methods for the detection and determination of thallium colorimetrically [1-3]. Feigl has described a colorimetric method for detecting traces of thallium by means of its color reaction with Rhodamine B [2]; the sensitivity of this method is 0.03 γ/ml Tl. Gurev [3], has used a colored solid phase reaction with methyl violet, proposed by V. I. Kuznetsov for detecting antimony and zinc [4,5], for determining thallium. The sensitivity of the method, according to Gurev's results, is 0.08 γ/ml Tl in a solution which is approximately 1 N with respect to HCl.

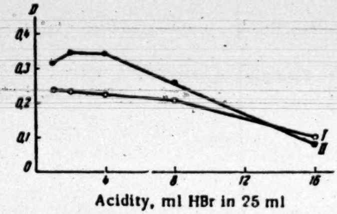


Fig. 1. Relation between optical density of colored thallium compounds and acidity of solution:
I) For methyl violet; II) for brilliant green

Colored solid phase reactions of the anions $TlCl_4^-$ and $TlBr_4^-$ with cations of basic organic dyes are of exceptional interest for determining traces of thallium, since, hitherto, we were unaware of more sensitive, and to a certain extent more specific, reactions for thallium.

We have studied the formation of the colored compound formed between the anion $TlBr_4^-$ and methyl violet under conditions where the acidity was varied, and found that the conditions chosen by S. D. Gurev are not the optimum ones.

The stability of the colored compound, which, according to V. I. Kuznetsov, is a salt of a complex metallohalide with the cation of a basic dye, depends to an appreciable extent on the acidity of the solution; the stability decreases appreciably with increasing acidity, as is evident from the graph shown on Fig. 1.

The results used for plotting this graph were obtained as follows: 5γ lots of Tl were introduced into 100 ml beakers; these were followed by 1, 2, 4, 8 and 16 ml of 1 N HBr respectively, and then 2 ml of bromine water added; the mixture was diluted with water to 20 ml and excess bromine removed by boiling. The solution, containing thallium as the anion $TlBr_4^-$, was transferred to a 25 ml measuring cylinder, and 2 drops of a 0.01% methyl violet solution and 5 ml amyl acetate added. Having stoppered the cylinder it was shaken vigorously; after 15-20 minutes the organic layer was removed and transferred to a photocolorimeter cell.

Optical density measurements were made on an FEK-M photocolorimeter using a green filter; ℓ = 10 mm.

As is evident from the graph, the optical density maximum is found when the acidity of the solution is 0.04-0.16 N with respect to HBr. The sensitivity of thallium determination at this acidity is 0.05 γ/ml Tl, i.e. almost twice that obtained under the conditions recommended by S. D. Gurev.

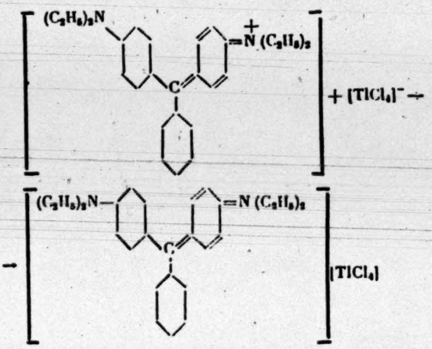
We used amyl acetate for extracting the colored compound, since the color in this solvent has a violet shade at any thallium concentration, whereas in benzene, at low thallium concentrations, the color has a bluish-violet shade, which has a definite effect on the accuracy of photometric measurements. The relation between optical density and concentration of thallium in 0.1 N HBr was also studied.

The relation is rectilinear; accordingly, the color intensity obeys Beer's law (Fig. 2) in the concentration range of thallium from 0.05-4.0 γ/ml. The proportionality does not hold above and below this limit, obviously, as a result of a decrease in the accuracy of measurements on the apparatus at low and high densities of the solutions.

The molar extinction coefficient was found to be 53,000 which is near to the value calculated by Gurev for various wavelengths (570 and 620 mμ). This value demonstrates the high sensitivity of the reaction when measurements are carried out on an FEK-M photocolorimeter with a green filter. The concentration change which leads to a change in light absorption of 0.01 is equal to 0.08 γ/ml.

Using the acidity which we chose we found it possible to determine hundredths and tenths of a microgram of thallium by using visual colorimetry. A difference in color in neighboring cylinders, for thallium contents within the range 0.05-0.5 γ/ml, is only observable on changing the thallium concentration in the two adjacent cylinders by a factor of 1.5 for a layer thickness of 3-5 cm. Experimental error in this case amounts to 16.5%. In addition, we studied reactions between $TlCl_4^-$ and $TlBr_4^-$ with another basic dye of the triphenylmethane series - brilliant green.

The large anions CNS^-, ClO_4^-, $Cr_2O_7^{=}$, $CrO_4^{=}$, $SbCl_6^-$, $TlCl_4^-$ form colored compounds with the cation of a basic dye; Kuznetsov [6] ascribes a salt-like character to these compounds:



These compounds can be extracted by organic solvents - benzene, toluene, xylene, amyl acetate, while brilliant green itself does not dissolve in these latter solvents. Benzene and amyl acetate proved to be the best solvents.

Effect of Acidity

The stability of the compound formed between thallium and the basic organic dye, as is clear from the example of the compound formed with methyl violet, depends to a large extent on the acidity of the solution. Accordingly, we first of all established the optimum acidity at which determination should be carried out.

Experiments were carried out as follows. 5γ lots of Tl were introduced into 100 ml beakers, and 1, 2, 4, 8, and 16 ml lots respectively, of 1 N HBr added; these lots were followed by 2 ml of bromine water, excess bromine was removed by boiling and the solutions finally transferred to 25 ml measuring cylinders; they were made up with water to 24 ml, and 1 ml of 0.01% brilliant green solution and 5 ml of amyl acetate added to each; the solutions were then stoppered and shaken. After 15-20 minutes the organic layer was run off into a photocolorimeter cell and the optical density of the colored solutions measured, using a red filter (l = 10 mm).

The results obtained are shown on the graph by Curves I and II (Fig. 1). Optimum acidity is at 0.08-0.16 N.

A consideration of Curves I and II shows fairly convincingly that the stability of the salt-like compound formed between $TlBr_4^-$ and brilliant green, depends on acidity to a greater extent than the stability of the analogous compound formed with methyl violet. The maximum of the optical density lies in a narrower acidity range (0.08-0.16 N).

Optical Properties

For establishing the relation between light absorption and thallium concentration, we measured the optical densities of solutions prepared by the method indicated above and containing from 0.05 to 5 γ/ml Tl, on a photocolorimeter fitted with a red filter.

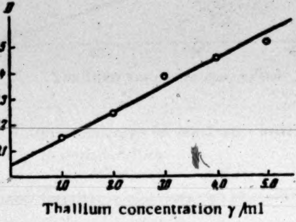


Fig. 2. Calibration curve for thallium + methyl violet; acidity 0.08 N HBr, ℓ = 5 mm; light filter, green.

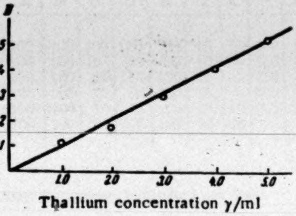


Fig. 3. Calibration curve for thallium + brilliant green; ℓ = 3.05 mm; light filter, red.

Results of the determination are shown on Figs. 2 and 3, from which it follows that the relationship between color and thallium concentration follows Beer's law for low and high thallium concentrations.

The molar absorption coefficient ϵ, calculated on the basis of these results, was found to be 70,000 for both cases. Such a high value for the molar absorption coefficient testifies to the high sensitivity of the reaction of the formation of dithizonates (ϵ = 50,000) and the sensitivity of the reaction between thallium and methyl violet (ϵ - 53,000).

TABLE 1

Concentration of thallium in γ ml	Optical density, D	Optical density, D	
		After 12 hrs	After 24 hrs
1.0	0.22	0.22	0.19
1.0	0.22	0.21	0.19
2.0	0.34	0.35	0.28
2.0	0.35	0.35	0.27
3.0	0.49	0.48	0.43

The sensitivity of the reaction of thallium with brilliant green is 0.03 γ/ml of Tl. For visual determination of 0.03-0.5 γ/ml Tl the difference in color of adjacent cylinders is completely satisfactory for a change in concentration of 1.5 times.

The color difference during photometric measurements, as can be seen from the curves on Figs. 2 and 3, amounts to 0.06 γ/ml.

We got good results by operating on an SF-4 spectrophotometer during determinations of hundredths of a microgram of thallium. The absorption maximum of the colored solutions lies at 630 mμ. The difference in color which can be measured corresponds to 0.0125 γ/ml (for changes in D of 0.02) on making measurements in vertical cells with ℓ = 1 cm. The color developed between thallium and brilliant green is fairly stable with time in the organic solvent (Table 1).

Excess of the organic dye has no effect on color intensity, since it does not dissolve in the organic solvents used – benzene and amyl acetate. It is sufficient to add 10 drops of 0.01% of dye solution for complexing 15 γ of Tl.

Effect of Other Elements

The following anions give colored salts with brilliant green: $Cr_2O_7^{2-}$, CrO_4^{2-}, $SbCl_6^-$, $SbBr_6^-$, $SnCl_4^{2-}$, $HgCl_4^{2-}$, $HgBr_4^{2-}$, ClO_4^-, CNS^-, $CdBr_4^{2-}$, $TlCl_4^-$, $TlBr_4^-$, $SnBr_4^{2-}$, WO_4^{2-}.

The anions MoO_4^{2-}, $BiBr_4^-$, $SbBr_4^-$, $CdCl_4^-$, $FeCl_6^{3-}$, $SnCl_6^{2-}$, as well as lead, zinc, manganese [2], copper [2], do not give colored compounds, and only in the presence of large excess of iron, copper, cadmium, lead, does a weak yellow-green color appear.

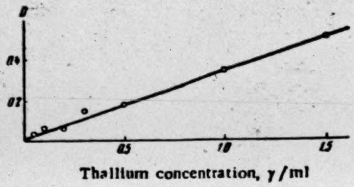


Fig. 4. Calibration curve for thallium + brilliant green: ℓ = 10 mm; red filter.

TABLE 2

Taken in mg							Thallium in γ	
Pb	Zn	Cd	Cu	Fe	Sb	Hg	Taken	Found
100	100	100	100	100	10	10	5.0	5.0
100	100	10	10	100	10	—	5.0	5.0
100	100	10	10	100	10	—	1.0	1.0
100	100	10	10	100	10	—	0.5	0.5
100	100	10	10	100	1	10	0.5	0.5
100	100	100	100	100	10	10	—	—

Most interfering elements can be readily removed from thallium by various published methods.

The effect of chromate and dichromate can be removed by addition of chromotropic acid, with which they form a compound which is not extracted by amyl acetate; the thiocyanate ion is destroyed on boiling with bromine and evaporating the solution to dryness. Antimony and tin can be removed by repeated evaporation to dryness of solutions containing concentrated hydrogen bromide and bromine.

Cadmium and mercury can be removed before oxidation of the thallium by bromine, by extracting their compounds with brilliant green with amyl acetate; univalent thallium, under these conditions remains in solution and can subsequently be determined after oxidation.

A good, though somewhat tedious method, is extraction of thallium bromide by ether from 1 N hydrogen bromide. Thallium is practically separated from all elements except gold by this method.

We determined the thallium content of synthetic mixtures after isolation of thallium bromide by ether extraction. The organic material in the ether extracts was destroyed by evaporating with sulfuric acid and hydrogen peroxide after removal of ether. Sulfuric acid was then removed by evaporating to dryness, 3 ml of 1 N HBr added, followed by 2 ml of bromine water; excess bromine was removed by boiling. The solution was transferred to 25 ml measuring cylinders, 1 ml of 0.01% brilliant green solution added, followed by 5 ml of amyl acetate; the colored compound was extracted, and then, after 20 minutes, measured colorimetrically.

Results are given in Table 2.

These results show that the amount of thallium found agrees with that taken. Negative results were obtained in blank tests (no thallium present).

SUMMARY

1. Solid color phase reactions between the anion $TlBr_4^-$ and the cations of the basic organic dyes – methyl violet and brilliant green – have been studied. At low acidity (0.04-0.1 N) these reactions can be used for colorimetric determination of hundredths parts of a microgram of thallium. The sensitivity of the reaction between thallium and methyl violet is 0.05 γ/ml, while with brilliant green it is 0.03 γ/ml Tl.

2. The optical properties of the colored compounds of thallium with methyl violet and brilliant green, respectively, have been studied.

3. The reaction with brilliant green is suggested as a new and highly sensitive reaction for determining thallium.

4. The content of thallium in complex mixtures has been determined by the method described.

LITERATURE CITED

[1] V. S. Fikhtengolts and N. P. Kozlova, Factory Labs. 21, No. 4, 407 (1955).

[2] F. Feigl, V. Gentil and D. Goldstein, Anal. Chim. Acta 9, No. 5, 393 (1953).

[3] S. D. Gurev, "Enrichment, metallurgy of non-ferrous metals and analytical methods," Collection, Scientific Trans. of State Institute of Non Ferrous Metals, No. 10 (Metallurgy Press, 1955), p. 371.

[4] V. I. Kuznetsov, J. Anal. Chem. 2, 179 (1947).

[5] V. I. Kuznetsov, J. Anal. Chem. 2, 373 (1947).

[6] V. I. Kuznetsov, Progr. Chem. 19, No. 1, 75 (1949).

Received March 24, 1956

BLANK
PAGE

SOME QUESTIONS RELATING TO THE TECHNIQUE OF RADIOCHEMICAL EXPERIMENTS

A. A. Goryunov

Novocherkassk Hydrochemical Institute

An Improved Protective Housing for Torsion Counters

In connection with the ever increasing application of the method of labelled atoms in chemistry, and the widening circle of people engaged in radiochemistry, we thought it would be a good idea to describe an improved construction for a protective housing for torsion counters. This construction in the main follows those more or less improved constructions described in the literature [1-4]. The improvements we have introduced relate to five points: 1) prevention of the possibility of accidental contamination by activity of the upper zone of the inner cavity of the housing; 2) facilitating cleaning from accidental contamination by the activity of the lower zone of the internal cavity of the housing; 3) the possibility of taking correct β-ray absorption curves; 4) convenience in mounting the torsion counter; 5) convenience of transport.

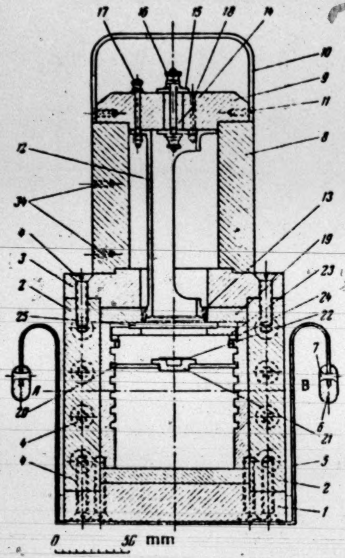
The first problem was solved by dividing the inner cavity of the protective housing into two parts: viz. the counting cell and the cell for the counter. The second problem was solved by constructing a freely removable counting cell - without dismantling all the housing - made of Plexiglas (on being withdrawn from the protective housing, the contaminated counting cell can be carefully washed or, in cases of heavy contamination, replaced). The third problem was solved by introducing a special frame with two flat springs, ensuring coaxial arrangement of the aluminum absorbers in the direct vicinity of the counter window. The fourth problem was solved by mounting the holder of the torsion counter on the top cover of the protective housing. Finally, the fifth problem was solved, on the one hand, by making the whole construction dismountable, while on the other hand a special basket with two handles was made for transporting it.

Since it is not possible, within the scope of a short article, to go into details on the construction of the protective housing, we have shown on Figs. 1 and 2, longitudinal and cross-sectional sections of it, while Figs. 3-8 are photographs which we hope will give a good idea of what it looks like as a whole and what its separate parts look like.

The wall of the protective housing is 25 mm thick; it is quite adequate for most work. The total weight of the housing, when the wall has this thickness, is ~35 kg.

A Set of Aluminum Absorbers and a Casing for Them

The most widely used method for identifying and checking on the radiochemical purity of radioactive preparations is the method of taking the absorption curves of β-radiation in aluminum. In order to be in a position to take absorption curves readily it is essential to have at one's disposal a set of 20-30 aluminum plates (absorbers), normally in the form of discs of varying thickness, covering the range 2 to ~2000 mg/cm^2 (0.01-7 mm). The thinnest absorbers (2,5,10 mg/cm^2) are cut from aluminum foil, and in order to prevent them from getting spoilt during use, they are glued on to flat rings of an accepted outside diameter (50 or 60 mm), cut from 0.5 mm of sheet aluminum. Absorbers up to a thickness of ~1000 mg/cm^2 can be cut from a suitable thickness of sheet aluminum with subsequent trimming to the requisite diameter and thickness on a lathe while the thicker absorbers can be turned wholly on the lathe. Final calibration of the absorbers thus prepared is carried out by weighing them on an analytical balance to an accuracy of 1 mg with subsequent division of the



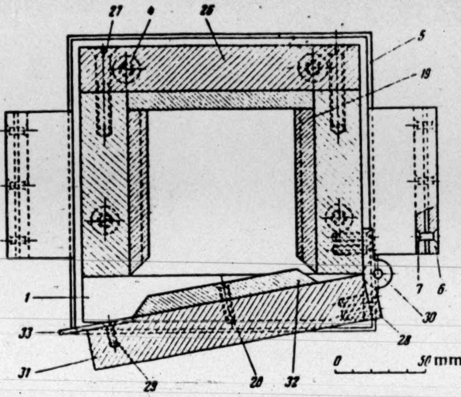


Fig. 2. Cross section of the protective housing taken along line AB (Fig. 1).
1) base (lead); 4) screw M8 x 40 mm (steel); 5) carrier (steel); 6) handle (wood or lexiglas); 7) rivet (copper); 19) lined box (Plexiglas); 26) back wall (lead); 27) screw M8 x 45 mm (steel); 28) screw M5 x 20 mm (steel); 29) screw M4 x 15 mm (steel); 30) loop (steel); 31) door (lead); 32) door lining (Plexiglas); 33) door handle (brass).

Fig. 1. Longitudinal section of the protective housing.
1) base (lead); 2) side wall (lead); 3) upper wall (lead); 4) screw M8 x 40 mm (steel); 5) carrier (steel); 6) handle(wood or Plexiglas); 7) rivet (copper); 8) cylinder (lead); 9) cover (lead); 10) frame (aluminum); 11) screw M4 x x 15 mm (steel); 12) counter holder (aluminum); 13) counter cover (aluminum); 14) insulating sleeve (polystyrene or Plexiglas); 15) insulating washer (polystyrene or Plexiglas); 16; inlet terminal for high voltage M4 x 55 mm (brass); 17) grounded terminal M3 x 55 mm (brass); 18) screw M3 x 55 mm (brass); 19) lined box (Plexiglas); 20) shelf (Plexiglas); 21) support under plate (Plexiglas); 22) plate (cellulose); 23) frame (Plexiglas); 24) spring (phosphor bronze); 25) aluminum absorber; 34) screws for fixing the shelves of the BGS block; M4 x 15 mm (steel).

weight thus found, expressed in mg, by the area of the disc, expressed in square cm. The result, which is in terms of mg/cm^2, is written, or better still embossed by means of a steel punch on the edge of each absorber. This set of absorbers can be conveniently stored in a vertical casing made of Plexiglas, which has a corresponding number of shelves and a plate for protecting them from dust. The front edge of each shelf should have a semicircular cut-away, in order that the absorber can be removed without hindrance from the shelf by means of a special type of tongs (Fig. 8). It goes without saying that the absorbers should not be handled by the fingers which may be contaminated; the absorbers should be always ideally clean. On Figs. 9 and 10, respectively, are shown the main features, and a photograph of such a container, which is suitable for absorbers 60 mm in diameter. In addition, in Table 1, we give the approximate values of the thickness of aluminum absorbers in linear and mass units, respectively, which gives on an approximate idea for independent preparation of a set of absorbers. In addition to the aluminum absorbers, it is also very useful to have a set of beryllium absorbers, by means of which it is possible to take more detailed absorption curves of soft β-radiation, or the initial stages of the absorption curves of harder radiation.

For relative measurements of the activity of samples possessing γ-radiation, it is often more convenient to carry out measurements on the basis of the γ-radiation rather than the β-radiation. For this purpose it is very useful to use a combined absorber-radiator, which consists of three small discs riveted together with small rivets;

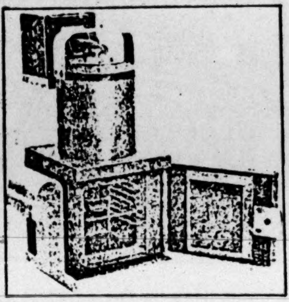


Fig. 3. General appearance of the lead protective housing.

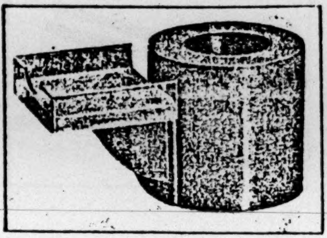


Fig. 4. Cylinder of the protective housing with a shelf for the BGS block.

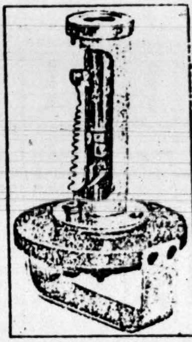


Fig. 5. Cover of the protective housing with the torsion counter holder fitted to it.

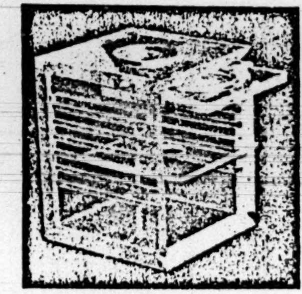


Fig. 6. Lined box of the protective housing made from Plexiglas.

two aluminum discs, 1700 mg/cm^2 (6 mm) and 200 mg/cm^2 (0.7 mm), and one lead one, 1800 mg/cm^2 (1.6 mm), fitted between the two aluminum ones. The purpose of the lower thick aluminum disc is to absorb all the β-radiation, coming from the measured sample, while the purpose of the lead disc is to create a flow of secondary electrons, which develop when γ-radiation from the sample passes through it. The top thin aluminum disc serves as a filter for the softest secondary β-radiation. When such a combination of absorber-radiator (a "sandwich" in English terminology) is used, a reasonable proportionality is observed between the intensity of the primary γ- and secondary β-radiation. A 31 tier Plexiglas container can be used for keeping the sandwich.

Celluloid Plates for Radioactive Samples. Pressforms for Preparing Plates

The most widely used material for making plates used in preparing samples for measurement of their radioactivity, is thin aluminum foil. Although this material is fairly easily obtainable and has good mechanical properties, it is still not suitable for preparing plates, since it has a completely unsatisfactory chemical stability. At the same time there is another cheap and readily available laboratory material which has excellent mechanical and chemical properties, which is almost ideal for preparing plates which can be used for measuring radioactivity. This material is none other than celluloid film, used for motion picture and photo film. After having been freed from the gelatin and the photographic emulsion distributed in it, by means of hot water, and cut into strips of the

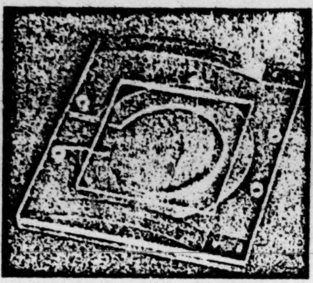


Fig. 7. Frame with springs for aluminum absorbers (Plexiglas and phosphor bronze).

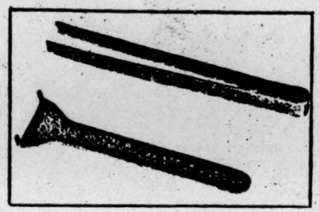


Fig. 8. Pincers for handling the aluminum absorbers and a "grip" for the frame and shelves (stainless steel or brass).

TABLE 1

Thickness of aluminum absorbers					
in mg/cm	in mm	in mg/cm	in mm	in mg/cm	in mm
4.0	0.015	130	0.5	600	2.2
8.0	0.03	140	0.6	700	2.6
10.0	0.04	185	0.7	810	3.0
16.0	0.06	210	0.8	900	3.3
21.0	0.08	240	0.9	1000	3.7
26.0	0.10	300	1.1	1200	4.5
34.0	0.13	350	1.3	1400	5.2
50.0	0.19	400	1.5	1600	5.9
79.0	0.3	460	1.7	1800	6.7
105.0	0.4	510	1.9	2000	7.4

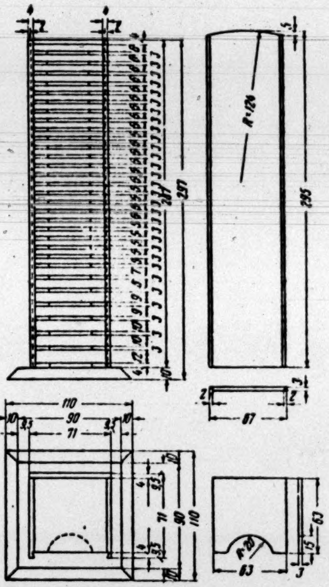


Fig. 9. Features of the vertical container for keeping aluminum absorbers (Plexiglas).

requisite width (or circles of the required size), this film is readily formed by means of a hand press heated to 120°. The preparation of such pressforms, whose construction is very simple, can readily be carried out in any workshop. Handling such pressforms does not require any special experience either. On Fig. 11 are shown the main features of two samples of similar pressforms of different diameter – 15 and 30 mm, while a photograph of one of them is shown in Fig. 12.

Pressforms can be heated on the usual type of electric hot plate with an open or closed heating element; in such cases, however, certain difficulties arise in connection with maintaining the requisite temperature, and it is not very suitable for forming plates. It is much more convenient to work with a special heater made from massive cast metal and provided with a small gage, low voltage heating element, supplied from an A.C. supply through a step-down transformer. The main features of such a heater are shown in Fig. 13, while Fig. 14 is a photograph of this heater.

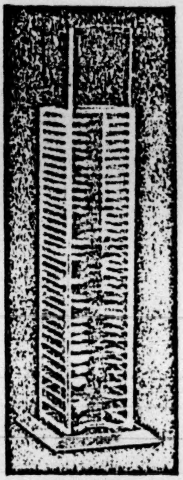


Fig. 10. General appearance of the vertical container used for keeping aluminum absorbers.

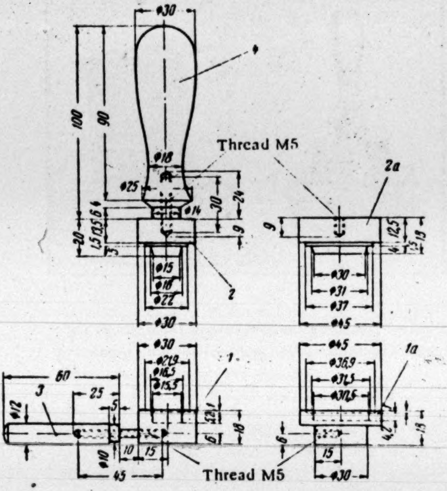


Fig. 11. Features of the hand pressforms used for forming celluloid plates.
1,1a) matrix (steel); 2,2a) die (steel); 3) matrix handle (wood); 4) handle of the die (wood).

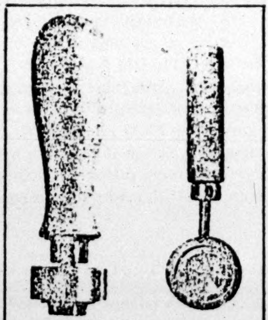


Fig. 12. General appearance of a hand pressform for forming celluloid plates.

The heating element is made from nichrome wire 0.6 mm in diamater. Two lengths of such a wire, each 1 meter long, are wound into two spirals 6 mm in diameter, and then connected in parallel, their ends being soldered to the ends of some copper leads with silver solder. The spirals are insulated from the body of the heater by means of mica or sheet asbestos; they are attached to the metal with liquid glass. The copper leads are insulated from the body of the heater by means of porcelain beads.

The porcelain block from a muffle furnace is very suitable as an insulating block for the inlet terminals. A block of this kind with 6 mm terminals ensures the necessary insulation of the lead-ins from the body, and allows one to pass a large current; it is fixed to the body by one screw.

The heater is supplied from an A.C. source through a 120 watt step-down transformer. The voltage in the secondary should be 12 volts, the permissible current 10 amperes. The voltage in the primary is controlled by means of a 300 ohm rheostat, calculated on the basis of a 1 ampere current, or an auto-transformer (LATR-1 or LATR-2).

A heater of the dimensions shown on the diagram attains the optimum temperature of 120° necessary for softening the celluloid at the same time as thermal equilibrium is reached with the surrounding material (with a temperature of 20°), when a voltage of 8.5-9 volts is applied to the terminals. Equilibrium is reached in 45-60 minutes. The thermal conditions necessary in any particular case can be conveniently established by measuring the temperature of some oil poured into the pressform by means of a mercury thermometer. Using such a heater

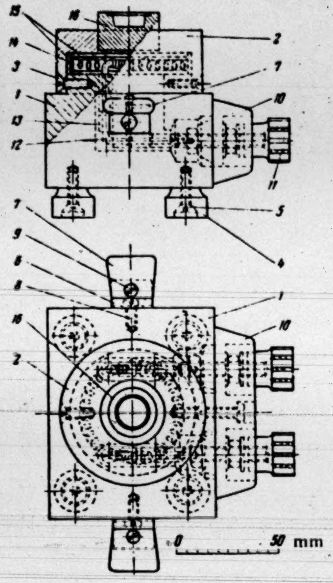


Fig. 13. Features of the heater of the pressform used for forming celluloid plates.
1) base (cast); 2) cover (cast); 3) screw M4 × 5 mm (steel); 4) knife (porcelain); 5) screw M5 × 25 mm (steel); 6) corner iron (steel); 7) handle (plastic); 8) screw M4 × 40 mm (steel); 9) screw M3 X 8 mm (steel); 10) insulating block (porcelain); 11) terminal (brass or plastic); 12) conductor (copper); 13) beads (porcelain); 14) heating spiral (nichrome); 15) insulation (mica or asbestos); 16) pressform matrix (steel).

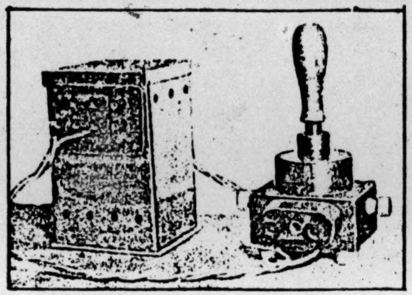


Fig. 14. General appearance of the heater for hand pressforms used for forming celluloid plates (a pressform is in position on the heater).

and hand pressform, it is possible to form 500-600 cellulose plates in 1 hour. On Fig. 15 are shown photographs of two types of plates formed by means of the devices just described. A plate 15 mm in diameter and 5 mm deep will take 1 ml solution. For samples of 0.03-0.05 ml (1 drop), smaller plates, or even flat discs, can be used.

It is very important to realize that despite the fact that celluloid is an extremely inflammable material, it can readily be heated up to 120-150° and, in this respect, is quite safe to handle, particularly if the samples placed on the plates are dried, not under 300 or 500 watt lamps as is often recommended, but in a special evaporator with an air stream, which has a comparatively low heating temperature. In an evaporator of this kind, which we shall describe in the next paragraph, the temperature in the working zone never exceeds 100°, and at this temperature the celluloid plates cannot catch fire; they are not even dedeformed.

An Evaporator for Drying Radioactive Samples

Radioactive samples are usually dried on plates of some material or other, under electric light bulbs placed at the focus of a suitable reflector [4]. Since, in such cases, with the object of accelerating drying, lamps of large power (200-300 watts) are used, which give off large amounts of heat and light, overheating of the samples often occurs with accompanying tendency to boil. As a result of this boiling up, partial sputtering of active material may occur, which leads to errors in measurement, and to contamination of the working place and air of the laboratory. Under such conditions, despite the expenditure of a large amount of energy, the drying rate remains rather low. In addition to the drawbacks already pointed out of this method of drying, one should also mention one other snag, viz. that as a consequence of strong heating of the surface of the working table, there often occurs loss of the linoleum covering which is sensitive to heating while, as a result of the brightness of the light, despite partial screening by the reflector, the eye gets tired.

All these snags can be overcome by drying the samples in a stream of warm air which has been heated in a special set-up by a low-voltage, relatively low power heater, e.g. automobile bulbs.

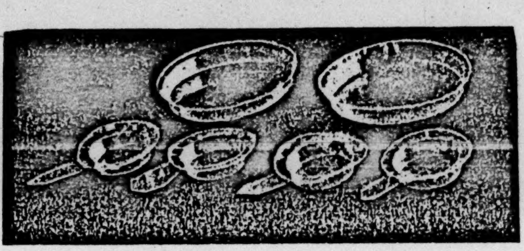


Fig. 15. Formed celluloid plates.

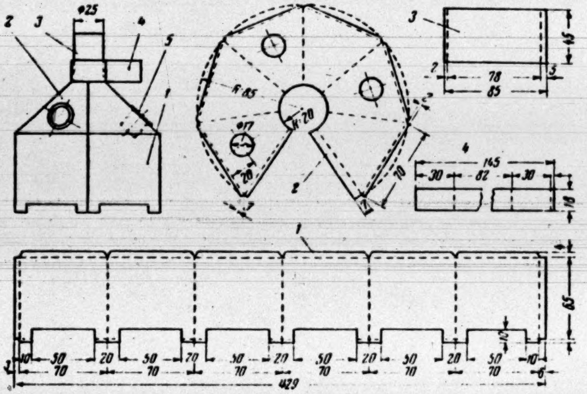


Fig. 16. General appearance and exploded appearance of the individual parts of an evaporator used for drying radioactive samples (stainless steel or white tin).

On Fig. 16 are shown the main features of such an evaporator, while on Fig. 17 is shown the photograph of the same simple set-up, which, operating on the principle already described, permits one to carry out a fairly rapid drying of radioactive samples at a temperature somewhat lower than 100°. It is in the form of a hexahedral sheath made of thin metal (0.3 mm), without a bottom but with a conical top finishing off at the apex of the cone in a short, wide, open tube. Into three alternate edges of the top of the sheath are fused bayonet sockets from automobile headlights, into which can be fitted 6-volt, 21-centiwatt, single contact automobile bulbs. The bulbs are connected in parallel, the frame of the apparatus itself acts as one of the poles, while the other pole is formed by the neutral contacts of the bulbs connected between themselves. The bulbs are supplied from an A.C. source via a 100-200 watt step-down transformer, whose secondary winding has a voltage of 6 volts and can be loaded with a 10 ampere current. In each of the six faces at the base of the sheath, from below, are made right-angled cut-outs, through which air from outside can pass into the apparatus. The air flow is maintained by the rising of the hot air up through the apparatus and out through the tube at the top, to be replaced by cold air coming in at the bottom.

The temperature developed by the automobile bulbs amounts to: a) 175° in the inter-bulb zone; b) 115° in the zone half way between the bulbs and the bottom surface of the apparatus; c) 95° in the lower part of the apparatus (operating zone).

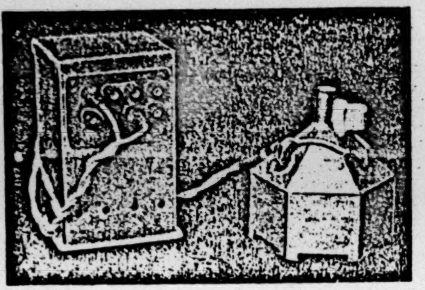


Fig. 17. General appearance of the evaporator for drying radioactive samples.

TABLE 2

Evaporation Rate of Samples of Distilled Water on Celluloid Materials

Sample volume in mg	On one plate, at the center, in minutes	On ten plates simultaneously
0.01	3.5	4.25
0.02	5.0	6.25
0.03	6.5	8.0
0.04	7.5	9.0
0.05	8.5	10.0
0.07	10.0	11.0
0.10	11.5	12.5
0.50	25	32
1.00	43	52

In Table 2 we have given results obtained during tests on the efficiency of such an evaporator; the test material was distilled water and it was evaporated from celluloid plates of the type described above. The first column gives the volume of water evaporated, the second column contains the results on evaporation rate of these samples from one plate placed at the center of the operating zone, while the third column contains similar information but on 10 plates (15 mm diameter) simultaneously, arranged round the periphery of the working zone. In all cases, in order to cut down on heat losses in reflection and radiation, the plates are placed on a lining covered with black paper. As is evident from Table 2, the evaporation rate of small samples is pretty high. It takes ~50 minutes to evaporate 1 ml. Evaporation rate from aluminum plates of the same shape is approximately 30% higher. This is the result of the fact that the aluminum absorbs heat rays to a greater extent, and is more strongly heated than celluloid, which is more transparent to heat rays.

SUMMARY

A number of auxiliary devices are described for the techniques of radiochemical experimentation. They include: 1) an improved protective housing for torsion counters; 2) a vertical container for aluminum absorbers; 3) celluloid plates; 4) pressforms and a heater for forming celluloid plates, and 5) an evaporator for drying radioactive samples.

These devices have proved their worth in practice and can be recommended for use in radiochemical laboratories.

LITERATURE CITED

[1] G. Hevesy, Radioactive Indicators (Foreign Lit. Press, Moscow, 1950).

[2] G. Friedlander and J. Kennedy, Introduction to Radiochemistry (Foreign Lit. Press, Moscow, 1952).

[3] V. Bochkarev, I. Keirim-Markus, M. Lvova and Ya. Pruslin, Measurement of β- and γ-Activity Sources (Acad. Sci. USSR Press, Moscow, 1953).

[4] V. I. Spitsin, P. N. Kodochigov, M. M. Golutvina, A. F. Kuzina and Z. A. Sokolova, Techniques Involving the Use of Radioactive Indicators (Acad. Sci. USSR Press, Moscow, 1955).

Received February 11, 1956

POLAROGRAPHIC DETERMINATION OF SELENIUM

V. F. Toropova

The V. I. Lenin Kazan State University

Selenium is usually determined polarographically by the electrical reduction of the selenate ion [1-5]. The reduction potential of quadrivalent selenium on a dropping mercury electrode, and the nature of the electrode processes, depend to a considerable extent on solution pH.

In the work described here we should like to propose a new polarographic determination of selenium, which is based on reduction of the seleno-sulfate ion ($SeSO_3^{=}$) on a dropping mercury electrode. Selenium, just like sulfur, but in contrast to tellurium, dissolves in concentrated solutions of alkali metal sulfites to form salts of seleno-sulfuric acid. Seleno-sulfate anions only exist in aqueous solution in alkaline media [6]; their capacity to be reduced under these conditions can be used for determining selenium in the presence of many anions. The aim of the present investigation was to study reduction of the seleno-sulfate ion on a dropping mercury electrode, and to study the possibility of using this reaction for the polarographic determination of selenium.

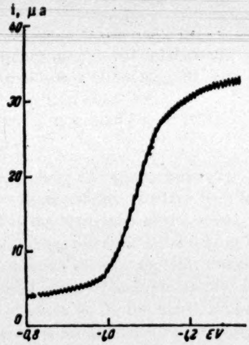


Fig. 1. Polarogram for 6.84 mM solution of Na_2SeSO_3 in 0.3 M $NaNO_3$ as supporting electrolyte.

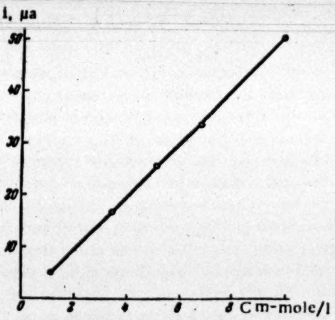


Fig. 2. Relation between wave height of $SeSO_3^{=}$ and its concentration.

We used a micropolarograph of the Heyrovsky type for the experimental work. The capillary characteristics were $m^{2/3} t^{1/6} = 1.31\ mg^{2/3} \cdot sec^{1/2}$ in 0.3 M $NaNO_3$ at -1.1 V. The anode was a saturated calomel electrode.

Sodium seleno-sulfate solution was prepared by dissolving red selenium in excess 10% sodium sulfite solution with slight heating. The solution was standardized by precipitating elemental selenium with the aid of hydrochloric acid, and then determining it gravimetrically. In the presence of sulfite ions, and at a pH not less than 10, $SeSO_3^{2-}$ concentration in solution remained constant for a long time.

Polarograms for a solution of sodium seleno-sulfate has the shape shown in Fig. 1. Maxima on the curves can be readily suppressed by adding a few drops of 1% phenolphthalein. The height of the polarogram wave is directly proportional to $SeSO_3^{2-}$ concentration as is evident from the curve shown in Fig. 2. The half-wave potential for $SeSO_3^{2-}$ is not a completely characteristic value, since with changes in concentration of the ions being reduced, the shape of the wave changes somewhat. In 0.005 M Na_2SeSO_3 solution in 0.3 M $NaNO_3$ as supporting electrolyte, $E_{1/2}$ –1.06 V with respect to the saturated calomel electrode. The half-wave potential of $SeSO_3^{2-}$ is independent of alkali concentration. In our experiments we varied hydroxyl ion concentration from 10^{-4} to $8 \cdot 10^{-2}$ g-ion/liter, but found no variation in reduction potential as a result.

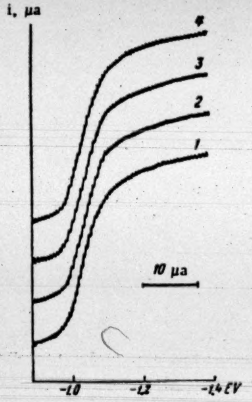


Fig. 3. Polarograms for a 5 mM solution of Na_2SeSO_3 in the presence of NaOH. OH^- concentration in g-ion/liter equal to: 1) 10^{-4}; 2) $8 \cdot 10^{-3}$; 3) $4 \cdot 10^{-2}$; 4) $8 \cdot 10^{-2}$.

TABLE

Results of Selenium Determinations

Solution concentration in M/l	Se taken in mg	i_d taken in microamps	Se found in mg
$3 \cdot 10^{-3}$	1.18	15.3	1.19
$6 \cdot 10^{-3}$	2.36	29.8	2.34
$9 \cdot 10^{-3}$	3.54	45.8	3.57

The corresponding polarographic curves are shown on Fig. 3. The dependence of the half-wave potential of the seleno-sulfate ion on hydroxyl ion concentration leads one to the only possible assumption on the mechanism of the electrode reaction:

$$SeSO_3^{2-} + 2e = Se^{2-} + SO_3^{2-}.$$

In order to confirm the correctness of this assumption we carried out electrolysis of a small volume of sodium seleno-sulfate solution (0.5 ml) using a rapid dropping capillary, according to a method suggested by Stromberg and Markacheva [7]. Since, during prolonged contact between metallic mercury and sodium seleno-sulfate solution, a black film forms on the mercury surface, the solution was separated from the mercury found in the lower part of the vessel, by means of a layer of chloroform. A blank test was carried out in parallel; i.e. during the same time that in the same vessel the mercury flowed from the capillary into a sodium seleno-sulfate solution without applying the potential. During electrolysis it was observed that the cathod wave of $SeSO_3^{2-}$ decreased while a black precipitate accumulated. At the same time, a small anode current was detected at a potential of –0.88 V. In the blank, no precipitate was formed, nor an anode wave observed. It follows that these phenomena are connected with electrolysis products. The half-wave potential corresponds to published values for the anode wave of the selenide ion under analogous conditions [8]. It is thus possible to conclude that one of the electrolysis products is the selenide ion which reacts with metallic mercury to form mercury selenide. This does not contradict the scheme put forward above for the electrode process. Formation of precipitate makes it more difficult for the ions to get to the dropping electrode. Accordingly, the polarographic wave for $SeSO_3^{2-}$ has a rather larger slope than is to be expected for a reversible two-electron reduction. The slope of the straight line drawn within the coordinates $\log \frac{i}{i_d - i} - E$ is equal to 0.06 instead of the theoretical value of 0.029. In strongly alkaline solutions of Na_2SeSO_3, probably for this very same reason, the polarographic wave splits into two.

Reduction of the seleno-sulfate ion on a dropping mercury electrode is an interesting case of an electrode reduction of sexivalent sulfur. The possibility of this happening, is probably determined, on the one hand, by the lower stability of the Se–S bond, as compared with that of S–S in thiosulfates, and with O–S in sulfates, and on the other by the exceptionally low solubility of mercury selenide.* The polarographic wave of $SeSO_3^{2-}$ is fully suitable for analytical purposes. We carried out determinations of selenium in sodium selenite. To a known volume of sodium selenite solution was added a small excess of thiourea, in order to get rid of elemental selenium. Solution plus precipitate was neutralized with sodium carbonate, and then sodium sulfite added till the red precipitate disappeared completely. The solution thus obtained was diluted with water in a 50 ml standard flask and the solution polarographed. The curve shown on Fig. 2 served as the calibration curve. Some results of the polarographic determination of selenium in sodium selenite are given in the table.

The method just described for determining selenium can be used also for other selenium containing compounds, which can be converted beforehand by normal methods into elemental selenium. Preparation of selenosulfates presents no difficulty.

SUMMARY

1. Reduction of the seleno-sulfate ion on a dropping mercury electrode has been studied. The scheme of the electrode process has been considered.

2. It has been demonstrated that it is possible to determine selenium polarographically as the selenosulfate ion.

LITERATURE CITED

[1] I. M. Kolthoff and J. J. Lingane, Polarography (State Chem. Press, Moscow, 1948).

[2] J. J. Lingane and L. W. Niedrach, J. Am. Chem. Soc. 71, 196 (1949).

[3] T. V. Arefeva and A. A. Pozdniyakova, from Symposium, Enrichment and Metallurgy of Non-Ferrous Metals (Metallurgy Press, 1953).

[4] B. Sandholc, Papir a celulosa. 8, 219 (1953); Abstracts J., Chem. (USSR) 1955, 19041.

[5] A. A. Shokol and S. A. Kacherova, Ukrain. Chem. J. 21, 89 (1955).

[6] F. Foerster, F. Lange, O. Drossbach and W. Seidel, Z. anorg. u. allgem. Chem. 128, 311 (1923).

[7] A. G. Stromberg and T. M. Markacheva, J. Phys. Chem. 28, 671 (1954).

[8] J. J. Lingane and L. W. Niedrach, J. Am. Chem. Soc. 70, 4115 (1948).

Received September 28, 1955

---

*Electro-reduction of $SeSO_3^{2-}$ consists, apparently, in a change from Se^0 to Se^2.

BLANK
PAGE

SPECTRA AND SPECTROPHOTOMETRIC ANALYSIS OF CHLORINATED ORGANIC COMPOUNDS

PART 1. DETERMINATION OF CHLOREX IN ADMIXTURE WITH DICHLOROETHANE

Ts. N. Roginskaya and A. I. Finkelshtein

Analysis of mixtures of chlorex (β,β'-dichlorodiethyl ether) and dichloroethane by chemical means is a very complex problem. Distillation of such mixtures, according to Engler, only leads to approximate results.

Very careful distillation requires a lot of time which complicates its use for production control.

Bearing in mind the rather large difference in the molecular structure of chlorex and dichloroethane, one would expect that one of the methods of molecular spectral analysis will give a solution of the problem. In order to choose the most convenient method, we carried out a detailed study of the spectrographic properties of chlorex; results of this study are given in the present article.

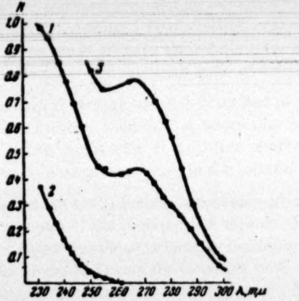


Fig. 1. Absorption spectra in the ultraviolet.
1) Chlorex in ethanol; 2) dichloroethane in ethanol; 3) chlorex in dichloroethane.

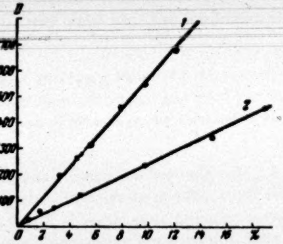


Fig. 2. Calibration curves:
1) On the basis of absorption in the ultraviolet (λ - 267.5 mμ); 2) on the basis of absorption in the infrared (λ - 8.50 μ).

We should like to point out that, in the literature available to us, there was only one paper [1], which gave the absorption spectra of a solution of chlorex in hexane in the ultraviolet. In our work chlorex of the following reagent grade was used: b.p. 175°; d_4^{20} 1.220; n 1.4562; published results d_4^{20} 1.220-1.222; n 1.4560-1.4570; b.p. 178.5°.

An SF-4 quartz photoelectric spectrophotometer was used for studying the absorption spectra and the analytical work in the ultraviolet. A detailed description of this apparatus, as well as of other Russian made spectrometers, used in our work, is given in the articles of Prokofiev [2], and Khrshanovsky [3], and is therefore not included here.

TABLE 1

Chlorex concentration in %		Error in %	
taken	found	absolute	relative
4.00	4,05	+0.05	1.25
13.30	13.0	—0.30	2.26
8.40	8.20	—0.20	2.38
7.40	7.25	—0.15	2.03
2.50	2.50	0	0
1.20	1.30	+0.10	8.35
1.62	1.70	+0.08	4.95
3.36	3.20	—0.16	4.75
4.63	4.35	—0.38	8.2
5.57	5,30	—0.27	4.85
7.95	7,75	—0.20	2.52
9,32	9.45	—0.37	3.77
12.12	15.75	—0.37	3.06
1.96	1.90	—0.06	3.06
3 98	3.85	—0.13	3.26

Mean relative error ~ 4.0

TABLE 2

Chlorex concentration in %		Error in %	
taken	found	absolute	relative
9.74	9.72	—0.02	0.20
3.98	3.90	—0.08	2.01
12.48	12.35	—0.13	1.0
7.65	7.75	+0.10	1.31
1.73	1.55	—0.18	10.4
6.02	6.02	0	0
12.96	12.90	—0.06	4 64
7.65	6.90	—0.75	0.98
6.65	6.80	+0.15	2.26
8.50	8.44	—0.06	0.70
4.90	4.92	+0.02	0.41
0.92	0.68	—0.24	26 0
3.81	4.25	+0.44	11.55
3.85	4.47	+0.62	16 1
9.31	9.72	+0.41	4.4

Mean relative error 5.5

Absorption spectra of chlorex in ethanol and dichloroethane respectively, and also those of dichloroethane are shown on Fig. 1. As shown in Fig. 1, absorption of a solution of chlorex in dichloroethane has a maximum at 267.5 mμ. Since dichloroethane does not give any appreciable absorption in this region, the wavelength just indicated can be conveniently used for analytical purposes. A calibration curve (Fig. 2) was constructed with the aid of synthetic mixtures. Results of the analysis of synthetic mixtures are given in Table 1. As can be seen from Table 1, the mean relative arithmetic error is ~ 4.0%. An analysis takes from 3 to 5 minutes; the sensitivity at a thickness of the absorbing layer of 1.0 cm amounts to 0.2%.

A drawback of the method just described in the impossibility of analyzing resinified samples or ones containing dissolved rubber. Removal of interfering impurities by absorption on activated charcoal was not successful. Consequently, in the case of resinified samples or ones contaminated by rubber, we developed an analytical method based on absorption spectra in the infrared.

We used an IKS-11 spectrophotometer with a rock-salt prism, and a potassium bromide cell 0.1 mm thick, for work in this part of the spectrum. A Nernst type lamp operating at a temperature of 1600-1700° served as source. Absorption spectra of chlorex in the infrared are shown in Fig. 3. Spectra were taken by successive registration of the absorption curve for an empty cell, and for the same cell containing test material. Slit width was controlled manually. Comparison of the spectra of chlorex and dichloroethane showed that the absorption band at 8.50 μ is the most suitable for analysis.

The calibration curve constructed on the basis of mixtures of chlorex and dichloroethane is shown on Fig. 2. Resins and dissolved rubber have no appreciable effect on the analytical results.

An analysis takes 15-20 minutes; the sensitivity is 0,3%; the mean relative arithmetic error is ~5.5%. Results of the analysis of synthetic mixtures are given in Table 2.

In the course of the work we also got combination scattering spectra and absorption spectra in the near infrared. Combination scattering spectra were obtained by means of the ISP-51 three-lens glass spectrograph, with a one-lamp illuminator, and standard glass light filter which isolates the Hg 4358 line used for exciting the spectra. Comparison of the spectra of dichloroethane and chlorex (Table 3), shows that combination scattering spectra, in principle, can be used for analysis.

For the study of the absorption spectra of chlorex and dichloroethane we used the universal monochromator UM-2 with two sulfur-lead photoresistances of type FS-A-1, incorporated in an unbalanced bridge scheme. Despite the small dispersion of the apparatus in this part of the spectrum, the results obtained (Fig. 4) are of

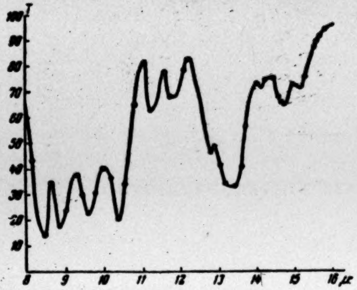


Fig. 3. Absorption spectra of chlorex in the infrared.

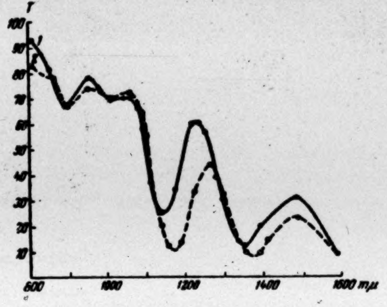


Fig. 4. Absorption spectra in the near infrared. 1) Chlorex; 2) dichloroethane (pure materials), thickness of the absorbing layer 3.0 cm).

TABLE 3

Combination scattering spectra		
chlorex	dichloroethane [4]	
242 cm^{-1} (1)	124 cm^{-1} (5)	1143 cm^{-1} (1)
295 cm^{-1} (1)	264 cm^{-1} (4)	1207 cm^{-1} (5)
671 cm^{-1} (10)	301 cm^{-1} (10)	1263 cm^{-1} (2)
757 cm^{-1} (3)	410 cm^{-1} (5)	1302 cm^{-1} (6)
792 cm^{-1} (1)	653 cm^{-1} (12)	1428 cm^{-1} (5)
1219 cm^{-1} (10)	676 cm^{-1} (5)	1442 cm^{-1} (4)
1258 cm^{-1} ($^1/_2$)	753 cm^{-1} (15)	2845 cm^{-1} (2)
1460 cm^{-1}	881 cm^{-1} (3)	2956 cm^{-1} (10)
2877 cm^{-1} (2)	943 cm^{-1} (5)	3002 cm^{-1} (6)
2916 cm^{-1} (2)	991 cm^{-1} (0)	
2968 cm^{-1} (7)	1032 cm^{-1} (2)	
3017 cm^{-1} (2)	1054 cm^{-1} (3)	

definite interest from the point of view of developing a simplified spectrographic method of analyzing chlorex-dichloroethane mixtures.

SUMMARY

1. Absorption spectra of chlorex in the ultraviolet, infrared, and near infrared have been taken, as well as combination scattering spectra.

2. A method has been developed for determining chlorex in mixtures with dichloroethane on the basis of light absorption in the ultraviolet and infrared.

LITERATURE CITED

[1] H. Mohler and F. Sorge, Helv. Chim. Acta 23, 1200 (1940).

[2] V. K. Prokofiev, Trans. All-Union Conference on Analytical Chemistry (Acad. Sci. USSR Press, Moscow, 1943), Vol. 2, pp. 175-187.

[3] S. A. Khrshanovsky, Leningrad University Bulletin (Leningrad, 1950), No. 3.

[4] K. Kolraush, Combination Scattering Spectra (Foreign Lit. Press, Moscow, 1952).

Received July 18, 1955

BLANK
PAGE

CHROMATOGRAPHIC SEPARATION OF Ni^{2+} AND Co^{2+} IONS

V. V. Oshchapovsky

Lvov Polytechnical Institute

Tsvet's chromatographic method [1], in all its forms, has found wide application in the most varied fields of chemistry and chemical industry.

Both natural and synthetic sorbents are used at present in chromatography. These sorbents, as a rule, do not possess selective action. Synthesis of resins exhibiting selective action [2], has, obviously, not yet gone beyond the confines of laboratory experimentation. Of definite interest in this respect, therefore, is the use of organic reagents as absorbents.

The mechanism of the action of such sorbents, boils down in all probability to chemical reaction between reagent and the ions being chromatographed. The products formed under such conditions, almost invariably, have different solubilities. It is just this difference in precipitate solubilities which is the basis of precipitation chromatography [3,4].

Of essential importance for separation by this method of precipitates, which are often colloidally dispersed, is the "cohesiveness" of the precipitates with respect to the carrier used, as often pointed out by T. B. Gapon and E. N. Gapon [5]. If the cohesiveness of the precipitate is high, then it will stay where it separates out, otherwise, it will creep down the column, thereby leading to poor separation. The use of organic reagents as sorbents permits one to achieve maximum cohesiveness, since the sorbent itself is a reagent-precipitant for one or several of the ions to be separated.

pH plays a very important role in the separation of ions on organic sorbents. Regulating the pH of the solution of ions to be chromatographed or of the eluant, and the use of masking complex formation, allows one to achieve selective action on the part of the sorbents, and to direct the absorption process.

The use of 8-hydroxyquinoline, cupferron, alginic acid, and other materials as absorbents for qualitative chromatographic analysis, and other purposes, has been described in the literature [6-8].

In the work described here a study was made of the use of dimethylglyoxime for the chromatographic separation of Ni^{2+} and Co^{2+} ions, and the application of this method of separation for analysis of cobalt preparations for nickel.

EXPERIMENTAL

Reagents. Experimental Procedure. Method.

In our experiments, unless otherwise stated, we used pure grade or analytical grade preparations of the corresponding salts. Cobalt salts – chloride and nitrate – which were completely free from nickel, were prepared from analytical grade reagent via the purpureo salt – chloropentamminocobaltichloride [9]. Preparations were used in which nickel could not be detected by a qualitative method suggested by Feigl [10].

The columns used for chromatography were glass tubes with internal diameter 3, 5, 8, and 12 mm. The lower part of the tube was drawn out into a short capillary 20-30 mm long and 1-2 mm in diameter. The overall length of the column was 100-150 mm. A plug of glass wool was fixed in the constricted part of the tube in order to keep up the adsorbent layer. Dimethylglyoxime, a specific reagent for nickel, was used as adsorbent.

Primary results showed that it is not convenient to work on columns filled with a long layer of reagent, since dimethylglyoxime is poorly wetted by solutions, and a long layer gives rise to considerable resistance to filtration. The use of pressure or vacuum for speeding up the throughput of solution proved inexpedient, since it did not lead to the expected results, but favored formation of filtration canals, rapid washing out of the adsorbent layer, breakdown of its homogenous packing, and, in the long run, to formation of a distorted chromatogram and breakthrough of the ion to be separated.

Accordingly, in the main, we used moist columns plus a short layer of adsorbent, the height of which was 10-20 mm, the weight of the dry material being 1-2 g. Even adsorbent density was ensured by precipitating it from a suspension in water in vertically fixed columns.

After preliminary tests we finally settled on the following procedure.

The solution prepared for filtration was introduced into the column, and under the weight of the column of liquid being filtered, sucked through a layer of dimethylglyoxime. The column was then washed with water till the filtrate was colorless and gave no reaction for Co^{2+}. When this was done a zone of nickel dimethylglyoximate separated out sharply; this was used for qualitative detection of nickel ions. The column was next washed with 0.1 N HCl, the nickel dimethylglyoximate was destroyed and the nickel dissolved, while the adsorbent was regenerated. In order to extract the nickel completely, and at the same time prepare the column for the next cycle of chromatographing, washing with water was carried out till the filtrate was neutral to methyl red. Filtrate and wash water were collected together. Ni^{2+} was determined in the solution obtained, colorimetrically [11]. A calibration curve was prepared with the aid of nickel sulfate.

It should be noted that regeneration of the adsorbent - decomposition of nickel dimethylglyoximate with 0.1 N hydrochloric acid – proceeds readily in the cold, only in the case of freshly formed precipitate, probably found still in a colloidally dispersed state. If the precipitate should age during separation, regeneration can only be effected by means of hot (50-70°), or more concentrated acid (0.5 N), since decomposition of a crystalline precipitate of $Ni(HDm)_2$* with hydrochloric acid in the cold is very slow [12]. During such regeneration, partial decomposition of dimethylglyoxime occurs, with formation of $CH_3COC(=NOH)CH_3$. This hinders formation of the colored complex of Ni^{2+} with dimethylglyoxime during colorimetric estimation, and requires an increase in the amount of oxidizing agent used.

For qualitative detection of Ni^{2+} we used micro columns of the dry type with an internal diameter of 3.5 mm. The length of adsorbent used in such columns was 3-6 mm, and weight of dry material 10-20 mg. The adsorbent was packed by gently tapping the lower end of the column on a hard object.

Effect of pH

We pointed out above the importance of pH in separation of ions on organic adsorbents. It was therefore of importance to check experimentally on the effect of pH, taking as an example the separation of Ni^{2+} and Co^{2+} ions on dimethylglyoxime as an adsorbent.

With this aim in view, we carried out several series of tests in which we studied the relation between the sensitivity of the reaction between nickel and dimethylglyoxime and pH, the effect of Co^{2+} concentration on the sensitivity of this reaction at various pH values, and the effect of pH on the separation of these ions.

The part played by the medium during the interaction of Ni^{2+} with dimethylglyoxime has already been pointed out by Chugaev [13]. In the literature (e.g. [14]) it is pointed out that fairly complete precipitation of nickel dimethylglyoxime can be achieved at a pH of 5-10. One would expect that these same conditions will ensure that the Chugaev reaction will have a maximum sensitivity when a chromatographic technique is employed too.

In order to verify this assumption we prepared a series of solutions of nickel sulfate in hydrogen phthalate and borate buffer solutions, respectively, covering the range pH 3.2-11. Ni^{2+} concentration in the stock solutions was $3.4 \cdot 10^{-4}$ mole/liter, which corresponds to 1 γ in one drop (0.05 ml). Less concentrated solutions were prepared by diluting the stock solutions with corresponding buffer solutions.

---

* H_2Dm = dimethylglyoxime.

TABLE 1

Relation Between Sensitivity of the Reaction of Ni^{2+} with Dimethylglyoxime and pH

pH	Nickel concentration in γ/drop					Notes
	1	0,2	0,1	0,075	0,05	
3.2	—	—	—	—	—	
4.2	+	+	—	—	—	
5.0	+	+	+	—	—	
6.0	+	+	+	+	—	
7.6	+	+	+	+	—	
8.0	+	+	+	+	—	Solutions are transparent up to pH 9
9.0	+	+	+	+	—	
10.0	+	+	+	+	—	Solutions are turbid
11.0	+	—	—	—	—	

Plus and minus signs denote whether a result was positive or not.

TABLE 2

Effect of Co^{2+} Concentration on the Chugaev Reaction at Various pH Values

Ratio	1 : 50				1 : 500				1 : 1000			1 : 5000	
pH	nickel content of one drop in γ												
	0.25	0.125	0.1	0.075	0.5	0.25	0.2	0.1	0.5	0.25	0.2	0.5	0.4
4.0	—	—	—	—	—	—	—	—	—	—	—	—	—
5.0	+	+	+	—	+	+	+	—	+	+	+	+	—
6.0	+	+	+	—	+	+	+	—	+	+	—	+	—
7.6	+	+	—	—	+	+	—	—	+	—	—	+	—
8.0	+	+	—	—	+	—	—	—	+	—	—	+	—

TABLE 3

Effect of pH on Separation of Ni^{2+} and Co^{2+} Ions

Solution pH	Ni^{2+} take in γ	Ni^{2+} found in γ	Notes
4	20	no absorption	
5	20	18.8 17.6 19.0	
6	20	19.8 18.0 20.1 20.3	
7,6	20	15.3 16.5 15.0	A precipitate rapidly forms in solution
8	20	15.0 16.0	

TABLE 4

Effect of the Ratio Ni:Co on Their Separation

Ratio Ni:Co	Ni^{2+} taken in γ	Ni^{2+} found in γ
1:50	20	20.5 20.7 22.0
1:500	20	20.8 20.0 18.3 20.2
1:500	50	47.0 49.9
1:1000	20	18.0 19.8 20.1 20.3
1:1000	50	45.5 47.8
1:3000	50	39.5 44.0 42.6

In individual experiments, one drop (0.05 ml) of each solution was transferred to a micro-column and allowed to soak in. The column was then washed with 2-3 drops of water and the adsorbent surface examined. Whether or not a positive result was obtained could be judged by the appearance, or the absence, of a rose colored zone of nickel dimethylglyoximate (Table 1).

It follows from Table 1 that the reaction has its highest sensitivity at pH 6-10. At a pH of 10, a turbidity develops in the solution; obviously, nickel hydroxide. This, however, has practically no effect on the sensitivity, since the hydroxide, under these conditions, is completely converted into nickel dimethylglyoximate.

In order to find out the effect of Co^{2+} concentration on reaction sensitivity, we prepared a series of solutions of cobalt salts in the buffer solutions indicated above; the cobalt salts were completely free from nickel. $NiSO_4$ was added to these solutions in such amount that the concentration of Ni^{2+} was 10γ/ml. The ratio Ni:Co varied within the limits 1:50 to 1:3,000, while the pH of the solutions was 4-8, since, already at a pH of 8, on standing, a turbidity developed after a time; this turbidity developed faster the lower the ratio Ni: Co, while at a pH of 9, at all ratios of Ni:Co, a copious precipitate with a rose color separated out. Less concentrated solutions were prepared by diluting the original stock solutions with the respective buffer solutions.

Experiments were carried out on micro-columns as described above.

Results of these experiments are given in Table 2.

The results given show that the reaction sensitivity is a maximum at a pH of 5-6; it drops somewhat on increasing the pH. The introduction of Co^{2+} into solutions of nickel salts lowers the sensitivity, and depresses the sensitivity the greater the amount of cobalt. On lowering the ratio of Ni:Co from 1:50 to 1:5,000, the limit of identification increased from 1.5-7 times as compared with results obtained in the absence of cobalt. The technique of precipitation chromatography, in which dimethylglyoxime is used as adsorbent, can be successfully used for separating very small amounts of nickel from large amounts of cobalt and for detecting Ni^{2+} in cobalt preparations of all grades. The reaction can be carried out more simply than as described by Chugaev [13] and Feigl [10] and is fully reliable.

In the next series of experiments a study was made of the separation of Ni^{2+} and Co^{2+} on moist macrocolumns. The method used has already been described. For this purpose solutions of cobalt salts prepared before, and containing 10 γ of nickel/ml, were used. The ratio of Ni:Co was equal to 1:1,000 which corresponds to the ratio of these elements in cobalt preparations of the analytical grade reagent.

These experiments confirmed that a pH of 5-6 is the optimum for separating these ions (Table 3).

The effect of the ratio Ni:Co on the separation of this pair of elements is clear from Table 4. These experiments were carried out with solutions whose pH was 6.

As these results show, separation of Ni^{2+} from Co^{2+} can be regarded as satisfactory. As one would expect, separation deteriorates with increasing values of the Co:Ni ratio. It is possible that this fact may be connected with the interaction of nickel dimethylglyoximate with cobalt ions, as a result of which the solubility of the precipitate increases. According to published results [15], the stability of the bond between Co^{2+} and dimethylglyoxime is higher than that of Ni^{2+} with the same compound; all the same, it is possible to separate nickel from large amounts of cobalt by means of the technique of precipitation chromatography.

Effect of Complex Formation

As already pointed out, cobalt salt solutions whose pH is higher than 7-8, are unstable and a rose precipitate separates out on not very long standing. In order to prevent formation of this precipitate we complex cobalt with tartrate ions.

Solutions were prepared as follows. Equal amounts of cobalt and tartrate salts, respectively, were dissolved in water. The solution obtained was made alkaline with ammonia until, on mixing one drop of this solution with one drop of an alcoholic solution of phenolphthalein on a watch glass, a raspberry color appeared. The nickel salt was added and the whole diluted with water till the nickel concentration was 10 γ/ml.

TABLE 5

Separation of Ni^{2+} and Co^{2+} from Tartrate-Ammonia Solutions at a pH of 9-10

Ratio Ni:Co	Ni^{2+} taken in γ	Ni^{2+} found in γ		
1 : 500	20	21.0	19.8	18.8
1 : 1000	20	18.0	18.4	19.8
1 : 3000	20	12.4	13.8	14.0

Chromatographic separation and subsequent operations and nickel determination were carried out as described already.

The results are given in Table 5.

It is clear that even in this case, separation of Ni^{2+} and Co^{2+} up to ratios of Ni:Co = 1:1,000 was satisfactory. The use of complex formation extends the pH limits at which it is possible to carry out separation of nickel and cobalt chromatographically.

We should like to point out that during work with solutions where the ratio Ni:Co was 1:3,000, formation of a dark brown solid crust in the column was observed. Formation of this crust slows down elution of Co^{2+} from the column considerably, and invariably led to loss of nickel.

The sensitivity of the reaction for nickel in these solutions at a ratio of Ni:Co of 1:500 was found to be 0.15 γ in one drop, while at ratios of from 1:1,000 to 1:3,000, the sensitivity was 0.2 γ.

Determination of Nickel in Cobalt Reagents

Determination of nickel in the presence of cobalt is known to be difficult. For this reason therefore, when reliable results are necessary, it is recommended that these metals be separated from each other prior to determination.

For large ratios of Co:Ni, some authors [6] recommend separation of these metals by extraction of nickel dimethylglyoximate with organic solvents, carried out under conditions where formation of this inner complex compound occurs.

We used chromatography for this purpose, taking dimethylglyoxime as the adsorbent.

Analytical Procedure

A sample of the preparation to be analyzed, taken in such amount that after dissolving it the solution should contain ~10-20 γ/ml, is dissolved in a suitable standard flask. The lower limit of the nickel concentration is determined by the sensitivity of the reaction. pH should be 6-10; accordingly the preparation should be dissolved in buffer solutions, e.g. acetate, or in the presence of tartaric acid with subsequent alkalization with ammonia to a pH of 9-10. 2-5 ml of the solution obtained is passed through a column containing dimethylglyoxime, at the rate of ~1 ml/minute. Such a throughput ensures free sucking of the solution through an adsorbent layer 15-20 mm long. The column is then eluted with separate lots, 2-3 ml each, of water, till a colorless filtrate is obtained which gives a negative reaction for cobalt with α-nitroso-β-naphthol. The nickel dimethylglyoximate zone is immediately destroyed with 0.1 N hydrochloric acid in the cold, and washed with water till the eluant gives a neutral reaction to methyl red. Filtrate and wash liquor are collected together in a standard flask; 10 ml of a freshly prepared 3% solution of ammonium persulfate is added, followed by 2-3 ml of a 1% solution of dimethylglyoxime in 5% alkali until the medium is alkaline. After 10-15 minutes, the volume is made up to the mark with water, the whole mixed and then measured colorimetrically, using a green filter. A calibration curve is drawn, using nickel sulfate. A determination takes about one hour.

In conclusion we give results for determination of nickel in several preparations of cobalt salts, which we obtained using this technique of separating nickel and cobalt chromatographically (Table 6). For comparison we have included the results obtained when the same preparations were analyzed by a State Standard Method, and also when these metals were separated by extraction of nickel dimethylglyoximate with chloroform.

The results obtained were satisfactory.

TABLE 6

Determination of the Nickel Contents of Cobalt Preparations

Preparation, grade	Ratio Ni:Co	Nickel content in %, determined by		
		State Standard Method*	Chromotographic separation	Separation by extraction
$CoSO_4 \cdot 7H_2O$ "pure"	1 : 210	0.163	0.155 0.156	0.150 0.145
$CoCl_2 \cdot 6H_2O$ "pure"	1 : 120	0.108; 0.114	0.113 0.110	0.124 0.119
$Co(CH_3COO)_2 \cdot 4H_2O$ "pure"	1 : 260	0.089; 0.084	0.085 0.086	0.085
$Co(CH_3COO)_2 \cdot 4HO_2$ **	1 : 2370	0.0103;0.0106	0.014 0.015	—
$Co(NO_3)_2 : 6H_2O$ "pure"	1 : 4060	0.00914	0 00894 и 0.00924	—

---

*Analysis of cobalt acetate was carried out by the State Standard Method stipulated for cobalt sulfate.

** "Analytical grade".

SUMMARY

1. It has been shown, using dimethylglyoxime as an example, that the use of specific organic reagents as adsorbents in chromatography can be effective for separation of certain ions.

This type of separation is an example of precipitation chromatography.

2. It has been shown that the efficiency of separation of Ni^{2+} and Co^{2+} depends on the pH of the solution of the ions to be separated chromatographically.

The use of complex formation enables one to extend the pH range of the solutions, in which nickel can be determined in the presence of large amounts of cobalt.

3. It has been confirmed that the greatest sensitivity of the Chugaev reaction for nickel is observed at a pH of 6-10.

The presence of Co^{2+} depressed the sensitivity of this reaction; nevertheless, 0.5 γ of nickel in a drop of solution can be detected reliably in the presence of a 5000-fold excess of cobalt.

4. A method has been developed for determining nickel in cobalt salts on the basis of a chromatographic separation.

LITERATURE CITED

[1] M. S. Tsvet, Trans. Warsaw Society of Naturalists; Biol. Section Vol. 14, p. 20 (1903).

[2] V. A. Klyachko, Proc. Acad. Sci. USSR 81, 235 (1951).

[3] T. B. Gapon and E. N. Gapon, Proc. Acad. Sci. USSR 60, 401 (1948).

[4] E. N. Gapon and I. M. Belenkaya, Colloid. J. 14, 5, 323 (1952) (T.p. 353).*

[5] The Chromatographic Method of Separating Ions, Collection of Articles, Edited by Prof. E. N. Gapon, Introductory article by E. Gapon and T. Gapon (Foreign Lit. Press, 1946).

[6] H. Erlenmeyer and H. Dahn, Helv. Chim. Acta 22, No. 6, 1369 (1939).

[7] F. M. Shemyakin and E. S. Mitselovsky, J. Anal. Chem. 3, 349 (1948).

[8] H. Specker and H. Hartkamp, Z. anal. Chem. 140, No. 3, 167 (1953).

---

*T.p. = C. B. Translation pagination.

[9] F. M. Perelman, A. Ya. Zvorykin and N. V. Gudima, Cobalt (Acad. Sci. USSR Press, Moscow, 1949), pp. 150-151.

[10] F. Feigl, Spot Analysis (State Tech. Press, Moscow, 1933), p. 293.

[11] A. M. Dymov and S. A. Volodina, Factory Lab. 12, No. 6, 534 (1946).

[12] A. K. Babko and P. B. Mikhelson, Ukrain. Chem. J. 18, No. 3, 265 (1952).

[13] L. A. Chugaev, Selected Works (Acad. Sci. USSR Press, Moscow, 1954), Vol. 1, pp. 58-61.

[14] V. N. Alekseev, A Course of Qualitative Chemical Semimicro Analysis (State Chem. Press, Moscow-Leningrad, 1952), p. 278.

[15] A. K. Babko and M. V. Korotun, J. Gen. Chem. 24, No. 4, 597 (1954) (T.p. 609).*

[16] E. B. Sandel, Colorimetric Determination of Metal Traces (State Chem. Press, Moscow-Leningrad, 1949), p. 354.

Received October 22, 1954

---

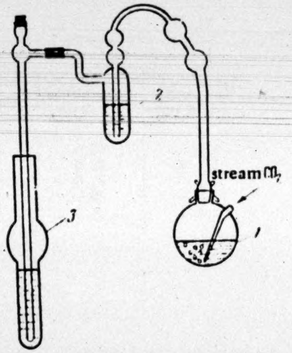
*T.p. = C. B. Translation pagination.

BLANK
PAGE

DETERMINATION OF SMALL AMOUNTS OF ALKOXY GROUPS IN SILICO-ORGANIC COMPOUNDS

S. V. Syavtsillo and E. A. Bondarevskaya*

A micro method of determining alkoxy groups (methoxy and ethoxy groups) in organic compounds is described in the literature [1,2], which is based on reaction with hydrogen iodide and formation of the alkyl halide, which is then absorbed by an alcoholic solution of silver nitrate. The amount of silver halide formed can be determined both volumetrically and gravimetrically. This method has been modified; in particular [3], it has been suggested that the alkyl halide formed be absorbed by a glacial acetic acid solution of bromine which contains sodium acetate, followed by subsequent determination of the iodine liberated.



Apparatus for determining ethoxy groups.

This technique has been used by Kreshkov and Nessonova [4], for determining large amounts of ethoxy groups in silico-organic compounds and in the tetramethyl and tetraethyl esters of orthosilicic acid. When butoxy groups are determined the conditions must be altered [5], since the butyl iodide formed during the reaction (b.p. 129.9°) boils at a higher temperature than hydrogen iodide (b.p. 127°), while formation of butyl iodide proceeds at a lower temperature. This complicates separation of butyl iodide and requires the use of step-like heating.

The aim of the work described here was determination of very small amounts (5.00 ± 0.01) ethoxy and butoxy groups in ethyl-phenylpolysiloxane compounds.

Determination of Ethoxy Groups

We used the apparatus shown in the diagram for determining ethoxy groups.

Kreshkov and Nessonova's method was modified in order to increase its sensitivity. Determinations were carried out as follows: an aliquot of test material** (0.02-0.015 g) contained in an ampoule was placed in reaction flask 1, to which had been added beforehand 3 ml of freshly distilled hydrogen iodide (sp. gr. 1.69-1.70). The ampoule was broken under the level of the hydrogen iodide. The reaction flask was sealed and connected with a wash bottle 2, filled to half its volume with a mixture of a 10% solution of $CdSO_4$ and $Na_2S_2O_3$, taken in the ratio 1:1. The exit tube of the wash bottle was immersed in a receiver 3 containing 4 ml of a 10% solution of sodium acetate in acetic acid and 5-6 drops of bromine. Before carrying out a determination, a weak current of carbon dioxide was passed right throughout the whole system; a micro burner was then used to take the temperature of the reaction flask and its contents slowly to the boiling point; heating at the boil was kept up for 45 minutes. At the end of this period the contents of receiver 3 were transferred quantitatively to a conical flask containing 1 g sodium acetate. A few drops of formic acid were then added till the color disappeared and there was no odor of bromine. 2 ml of sulfuric acid (1:4) was next added, followed by 1 ml of 10% potassium iodide solution, and the liberated iodine titrated with 0.02 N $Na_2S_2O_3$. A blank was run in parallel. Calculations were made by means of the formula.

---

*R. M. Potsepkina carried out some of the experimental work.

**If the material does not dissolve in hydrogen iodide, phenol is added.

$$\% \text{ alkoxyl} = \frac{a \cdot b \cdot 100}{k}$$

where a is the amount of ethoxy or butoxy groups in mg corresponding to 1 ml of 0.02 N $Na_2S_2O_3$; b the amount of 0.02 N $Na_2S_2O_3$ used in ml; k the weight of sample in mg. The results obtained are given in Table 1.

TABLE 1

(OC_2H_5)groups taken in %	(OC_2H_5)groups found in %	Relative experimental error in %
0 012	0.012	0
0.120	0.129	+7
0.409	0.422	+4.2
0.850	0.846	—0.5
0.860	0.846	—1.5

The results in this table show that the sensitivity of the determination is 0.01%, while the accuracy of ethoxy group determination is 7% relative. Ethoxy group contents varying from 0.01 to 0.8% were determined in ethylpolysiloxane compounds by the method indicated.

Determination of Butoxy Groups

Butoxy groups were determined in the same apparatus as that used for determining ethoxy groups. In order to ensure complete distillation of the butyl iodide formed, step-wise heating of the sample with hydrogen iodide was adopted. This was achieved by slowly raising the temperature in the course of the first 30 minutes to 40°, then for the next 30 minutes to 60°, followed by a rise to 100° in the course of another 30 minutes; finally carbon dioxide was passed through the apparatus for 15-20 minutes. All further operations were the same as those described already for ethoxy groups. Using this method we determined the butoxy group content of the tetrabutyl ester of orthosilicic acid and of synthetic mixtures of this ester with ethylpolysiloxane polymer not containing butoxy groups. The results obtained are given in Table 2.

TABLE 2

(OC_4H_9)groups taken in %	(OC_4H_9)groups determined in %	Relative experimental error in %
0.10	0.09	—11.0
0.24	0.26	+ 7.7
0.26	0.24	— 7.7
0.69	0.64	— 7.2
1.36	1.50	+ 9.5

From these results it is clear that the sensitivity of butoxy group determination is 0.1%, while the accuracy is 11% (relative). This method was used for analyzing vinylpolysiloxane resins for their butoxy group contents, ranging from 0.5-0.6%.

SUMMARY

A micro method has been developed for determining small amounts of ethoxy and butoxy groups in polysiloxane compounds. The sensitivity of the method is 0.01%. The accuracy is 10% relative.

LITERATURE CITED

[1] A. Friedrich, Practice of Quantitative Organic Micro Analysis (All-Union Sci. Tech. Press, 1939).

[2] F. Pregl, Quantitative Organic Micro Analysis (State Chem. Press, 1934).

[3] F. Viebock and C. Brecher, Ber. 63, 3207 (1930); R. Bournique and A. Raymond, Analyst 43, No. 2, 40 (1954).

[4] A. P. Kreshkov and G. D. Nessonova, J. Anal. Chem. 4, 220 (1949).

[5] Bulletin, Exchange of Experience in the Lake-dye Industry (State Chem. Press, 1953); K. Burnik, Abstracts J., Chem. (USSR) 1955, No. 14, 236.

Received April 2, 1955

DIRECT POTENTIOMETRIC TITRATION OF THE SULFATE ION USING THE Mo | MoO$_3$ ‖ BaSO$_4$ INDICATOR ELECTRODE

PART 1.

A. D. Miller

The Lensovet Leningrad Technological Institute

Attempts at using the Pb/PbSO$_4$ electrode as indicator electrode for direct determination of the sulfate ion have proved unsuccessful [1]. Kolthoff and Fourman [2] reckon that "there is no satisfactory electrode for the sulfate ion." Indirect methods of carrying out potentiometric determination of sulfate [2-11], have a number of drawbacks (neutrality of the medium, absence of coprecipitating cations and salts, possessing buffer properties), which render them of little use in practice. Direct titration of sulfate with barium chloride, in which the end point is shown by a change in pH near the equivalence point also has the drawbacks enumerated above. It is known that any solid phase is capable of adsorbing both positive and negative ions, as a result of residual valency forces. Fajans [12] and coworkers established the rule which ionic adsorption follows.

Batchelder and Meloche [13] found that the pH of the medium changes during precipitation of sulfate by barium chloride; they found that during potentiometric titration with an electrode sensitive to pH changes, it is possible to determine the sulfate ion. On the basis of the work of Fajans and on that of Frumkin and coworkers [14], Batchelder and Meloche explained the pH changes before and after the equivalence point by hydrolysis of the adsorbed complexes formed. Other research workers [15,16] came to similar conclusions.

If insufficient precipitant is present, hydrolysis of the adsorbed complex can be represented by the reaction:

$$(BaSO_4)_x)(SO_4^{2-})_y \mid Na_{2y}^{+} + 2yH_2O \rightleftarrows (BaSO_4)_x\,(SO_4^{2-})_y \mid H_{2y}^{+} + 2yNa^{+} + 2yOH^{-}.$$

while if excess precipitant is present, the reaction is

$$(BaSO_4)_x\,Ba_z^{2+} \mid Cl_{2z}^{-} + 2zH_2O \rightleftarrows (BaSO_4)_x\,Ba_z^{2+} \mid (OH^{-})_{2z} + 2zH^{+} + 2zCl^{-}.$$

The result of hydrolysis according to the first scheme is the appearance of free alkali, according to the second scheme – acid.

We made use of the specific sorption properties of barium sulfate for Ba^{2+} and SO_4^{2-} ions, for making a new indicator electrode which could be used for potentiometric titration of sulfate, and which is sensitive to changes in concentration of SO_4^{2-} and Ba^{2+} ions near the equivalence point.

It has been suggested that any suitable conductor of an electric current, covered with a sufficiently dense and fine layer of barium sulfate can be used as an electrode of this type.

Changes in the reaction and discharge of the sorbed complex on the electrode surface, during the change-over from excess SO_4^{2-} ions (before the equivalence point) to excess Ba^{2+} ions (after the equivalence point), according to the scheme

$$(BaSO_4)_x\,(SO_4^{2-})_y \rightarrow xBaSO_4 \rightarrow (BaSO_4)_x\,Ba_z^{2+},$$

would appear to be the only cause of the potential jump, and it should be possible to carry out titration in acid media also, i.e. the method might be free of all the drawbacks inherent in the method of adsorption-hydrolytic titration.

Electrodes made directly from the metal or by subsequent chemical treatment of nichrome, tantalum, and tungsten rapidly deteriorated during sulfate determination, on account of the weakness of the bond between surface layer and metal.

It was established that, by oxidative treatment of molybdenum followed by treatment with barium salts and sulfuric acid, it was possible to prepare an electrode with stable cohesion of the type: metal|oxide|$BaSO_4$.

A molybdenum wire ~1 mm in diameter with two to three turns on the end (diameter of a turn, 3-4 mm, interval between turns, 2.5-3.0 mm), was strongly heated to a white heat in the oxidizing flame of a Teklu burner and then immersed in molten sulfur; it was again strongly heated and rotated at the same time. The sulfur which has formed a surface film of sulfide and is readily oxidized during the annealing, favors the formation of a substantial layer of molybdenum oxides. This operation was repeated 3-4 times, after which the wire was annealed without subsequent immersion in sulfur, but immersed (while still hot) as rapidly as possible in a saturated solution of $BaCl_2$ or $Ba(OH)_2$.* Alternate annealing and immersion in $BaCl_2$ solution was repeated 22 times; the last two times the electrode was allowed to cool before immersion. The electrode was rotated all the time that annealing was carried out. The electrode was next annealed continuously for not less than 10-15 minutes in the hottest part of the burner flame. The cooled electrode was next immersed for a few minutes in 0.2 N H_2SO_4, after which it was transferred to a fresh solution of 0.2 N H_2SO_4 and left there for several hours. The electrode was finally stored in 10^{-3} N Na_2SO_4. Electrodes which have deteriorated may be restored by repeating the cycle of immersion and annealing 5-6 times (without removing the old surface layer), and finally finishing up as usual; good results were obtained with electrodes restored this way.

Titration of the Sulfate Ion with the $Mo|MoO_3 \| BaSO_4$ Indicator Electrode

The first experiments on potentiometric titration of sulfate ions with the $Mo|MoO_3 \| BaSO_4$ electrode were carried out on the basis of a compensation scheme. The null-instrument had a sensitivity of $2 \cdot 10^{-8}$ amp. 0.1 N solutions of Na_2SO_4 and $BaCl_2$ were used for titration. On Fig. 1 are shown two titration curves obtained with one electrode of the type indicated. Curve I shows the form taken by the titration curve in a neutral medium, while Curve II shows the shape of the curve in a weak hydrochloric acid medium (0.025 N). In both cases satisfactory agreement was obtained with the results of gravimetric analysis.

The value of the potential jump depends on the quality of the electrode. The curves shown on Fig. 1 relate to one of the first electrodes. At the equivalence point, during titration in a neutral medium, $\Delta E/\Delta V$ is 60 mv/ml, while in 0.025 N HCl, the value is 30 mv/ml.

The following characteristics were noted during titration in neutral and acid media:

1. The value of the potential jump at the equivalence point is appreciably smaller in acid than in neutral media, but the titration curve is suitable for observation, and titration is quite feasible.

2. The sign of the charge of the indicator electrode with reference to the calomel electrode, is negative in neutral media and positive in acid media.

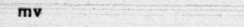


Fig. 1. Two titration curves taken with the same electrode.

---

*Reaction between BaO and MoO_3 starts at 290° [17].

3. The potential jump on the titration curve at the equivalence point is opposite in direction in neutral and acid media, respectively. In neutral media there is a potential drop, while in acid media it is a step-up.

Uncompensated Titration with a Bimetallic Pair of Electrodes

A tungsten wire was used as the reference electrode in almost all tests when titration was carried out according to this scheme.

During work with a bimetallic pair of electrodes, in both neutral and acid media respectively, the same characteristics were observed as during titration by the compensation method using the calomel electrode as reference electrode.

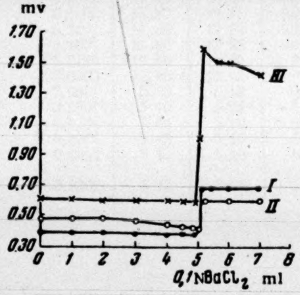


Fig. 2. Three titration curves with the same indicator electrode, using an uncompensated setup.

On Fig. 2 are shown three titration curves with the same indicator electrode when the uncompensated scheme was used. Curve I illustrates the titration curve obtained in acetic acid media (0.1 N) when an external resistance of 30,000 ohms was used; Curve II – the curve obtained during titration in a hydrochloric acid solution (0.02 N with respect to HCl), and using an external resistance of 30,000 ohms; Curve III – that obtained in the same hydrochloric acid medium but using an external resistance of 1,000 ohms. In all three cases, as is evident from the curves themselves, there was observed a clear cut jump at the equivalence point (±0.05 ml). At high values of the resistance, the potential is established quicker; nevertheless, it is convenient, for observation, to select a resistance such that the jump at the equivalence point is not less than three small divisions on the millivoltmeter* (0.3 mv). The shape of the curves is suitable for visual titration.

Effect of Sulfate Ion Concentration, Acidity of the Medium, and Other Salts, on Accuracy of Titration

The relation between the position of the equivalence point and SO_4^{2-} concentration in the presence of other (indifferent) salts is shown in Table 1.

The media were 0.02 N with respect to HCl, except where otherwise specifically stated. All determinations, except two, were carried out by means of the uncompensated method using a bimetallic pair of electrodes (reference electrode – tungsten). The concentrations of the original Na_2SO_4 and $BaCl_2$ solutions were established gravimetrically. Na_2SO_4 solutions measured from a buret were diluted with different amounts of water. In the first column of Table 1 the normality of the Na_2SO_4 solutions after dilution is given.

It is clear from Table 1 that a change in sulfate ion concentration from 0.008 to 0.100 N has practically no effect on the position of the equivalence point.

At the SO_4^{2-} concentrations indicated, experimental error was found to be within the limits of ± 1%.

The presence of the chlorides of sodium, ammonium, and potassium amounting to 150 g/liter had no effect on experimental accuracy (the last 5 experiments in Table 1).

Table 1 also contains the results of three experiments on titration in acetic acid media. Acetic acid concentration could be increased to 0.5 N without affecting titration accuracy. Hydrochloric acid shows a very marked effect on the value of the potential jump at the equivalence point (Table 2).

Increasing the HCl concentration does not lead to a displacement of the position of the potential jump relative to the true equivalence point; nevertheless, the value of the jump drops sharply.

The HCl concentration should not exceed 0.05 N if reliable results are to be obtained.

---

*During work with a noncompensated setup a millivoltmeter with a scale of 17 mv was used.

TABLE 1

Effect of Sulfate Ion Concentration and Certain Salts on Titration Accuracy

Normality of Na_2SO_4 solution	$BaCl_2 \sim 0{,}1\ N$		Error in %	Observations
	amt. that should be used in ml	amt. actually used in ml		
0.0083	4.95	4.99	+0.80	
0.0167	19.80	19.95	+0.75	
0.0167	19.80	19.70	−0.50	
0.0333	14.85	14.75	−0.65	
0.0601	19.80	19.65	−0.75	
0.1002	29.70	29.65	−0.20	
0.1002	19.80	19.85	+0.25	Concentration of HCl 0.035 N
0.1002	19.80	19.88	+0.40	Compensated method with calomel electrode
0.1002	19.80	19.68	−0.60	
0.0700	19.80	19.80	0.00	0.3 N CH_3COOH medium
0.0700	19.80	19.93	+0.70	0.5 N CH_3COOH medium
0.0301	5.10	5.10	0.00	
0.0301	5.10	5.05	−1.00	50 g/liter of NaCl added
0.0301	5.10	5.10	0.00	50 g/liter of NH_4Cl added
0.0301	5.10	5.10	0.00	50 g/liter of KCl added
0.0301	5.10	5.10	0.00	50 g/liter of NaCl added. Medium 0.2 N CH_3COOH
0.0301	5.10	5.05	−1.00	Mixture of various amounts of NaCl + NH_4Cl + + KCl, total amount 150 g/liter, added.

TABLE 2*

Effect of Hydrochloric Acid Concentration on the Value of the Potential Jump

Normality of HCl	0.02	0.05	0.07	0.10	0.40
Value of the potential jump in mv	0.41	0.48	0.33	0.20	0.00

Suggested Mechanism for the Electrode's Operation

The Mo|MoO_3|$BaSO_4$ electrode should be sensitive to changes in concentration of both SO_4^{2-} and Ba^{2+} ions, respectively, near the equivalence point, as a result of the specific sorption of these ions by the surface layer of $BaSO_4$.

A few research workers have used the sorptive capacity of barium sulfate crystals for SO_4^{2-} and Ba^{2+} ions for titration, based on a secondary hydrolysis reaction of the sorbed complex, and on changes in pH of the surrounding medium which occur as a result of this hydrolysis, and which it would be impossible to observe in the presence of free acid or buffer salts respectively.

In our case the very reaction of formation of the sorbed complex on the surface of the electrode is the reason for the formation of a double electric layer and, consequently, of the development of a potential, while the potential jump at the equivalence point is determined by the breakdown of the complex initially formed, and the formation of a new one which is oppositely charged.

In this case, hydrolysis is of no significance and, as has been shown, titration can proceed quite well in acid media.

Near the equivalence point, during titration of a sulfate with a barium salt, the changes which occur on the surface of the Mo|MoO_3|$BaSO_4$ electrode can be expressed by the scheme:

$$[(BaSO_4)_x\,(SO_4^{2-})_n] \rightarrow BaSO_4 \rightarrow [(BaSO_4)_x)\,Ba_z^{2+}].$$

On Fig. 3 are shown curves obtained during direct and back titration respectively, using an uncompensated setup, and the same indicator electrode. The continuous line represents the change in potential during titration of sulfate with barium chloride in a weak hydrochloric acid medium, while the dotted line represents potential changes during back titration.

---

*Uncompensated scheme with bimetallic pair Mo| MoO_3| $BaSO_4$ – W.

For direct confirmation of the suggested scheme of changes in charge on the surface of the Mo|MoO_3|$BaSO_4$ electrode, experiments were carried out on determination of the charge on very small crystals of $BaSO_4$ obtained: 1) when insufficient precipitant (barium salt) and 2) excess barium salt, respectively, were present. Suspensions of the barium sulfate crystals were subjected to electrophoresis at a voltage of 110 V. The apparatus and technique normally used for determining the charge of colloidal particles were used [18]. Results of these experiments confirmed the assumption on formation of a charged complex; in the first instance $BaSO_4$ crystals carried on themselves a negative charge, while in the second they carried a positive charge and, since both in the first and in the second case, barium chloride was added to the sulfate, then without a doubt, overcharging of the complex occurs during titration.

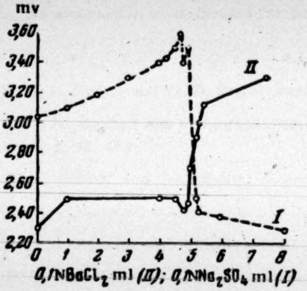


Fig. 3. Direct and back titration, respectively, on an uncompensated setup.

The reason for the difference in character between the titration curves near the equivalence point in acid and neutral media, respectively, can be explained in the light of the ideas expounded above. In neutral media, the sign of the charge of the indicator electrode with respect to the calomel or tungsten reference electrodes, respectively, is negative. When the equivalence point is reached, as a result of overcharging of the indicator electrode

$$[(BaSO_4)_x\,(SO_4^{2-})_y] \rightarrow [(BaSO_4)_x Ba_z^{2+}],$$

its positive potential increases, but all the same, remains negative with respect to the reference electrode. As a result of the approximation of the potential of the indicator electrode from the region of strongly negative values to the null value of the reference electrode potential, the potential difference between them decreases; this is expressed by the lower branch of the titration curve. In acid media, the position is different. The electrode Mo|MoO_3|$BaSO_4$ to a certain extent is an oxide-metallic electrode. The oxidation-reduction potential of such an electrode will depend on hydrogen ion concentration

$$2MoO_3 + 2e + 2H^+ \rightleftarrows Mo_2O_5 + H_2O.$$

We established, by means of specially conducted experiments, that the electrode Mo|MoO_3|$BaSO_4$* can be used as an indicator electrode during titration of acid by alkali. In the course of the work it was observed that during titration of sulfate in acid media, the potential of the indicator electrode was always positive with respect to the calomel or tungsten reference electrodes, respectively. Nevertheless, on the surface of the indicator electrode, at the moment when equivalence is obtained, there occurs overcharging of the sorbed complex, as in neutral medium:

$$\left[(BaSO_4)_x\,(SO_4^{2-})_y\right] \rightarrow [(BaSO_4)_x Ba_z^{2+}].$$

The positive potential of the indicator electrode increases but, since right from the beginning to the end of the titration the indicator electrode potential is positive with respect to the reference electrode, the measured difference between indicator electrode and reference electrode increases; this is expressed by a rise in the titration curve.

---

*Or simply Mo|MoO_3.

SUMMARY

1. The electrode Mo|MoO_3|$BaSO_4$ is suitable for practical determination of the equivalence point during titration of sulfate ions by barium ions; this electrode is obtained by alternate annealing and quenching in a solution of barium chloride, of a molybdenum wire, followed by subsequent treatment with sulfuric acid.

2. The suggested method of potentiometric titration of sulfate with the indicator electrode Mo|MoO_3|$BaSO_4$ can be used both in neutral and acid media, using both classical and uncompensated (with bimetallic pair of electrodes) schemes of titration.

3. An explanation is put forward for the mechanism of the Mo|MoO_3|$BaSO_4$ electrode.

LITERATURE CITED

[1] I. I. Zhukov and Ts. G. Raichinshtein, J. Gen. Chem. 4, 962 (1934).

[2] I. M. Kolthoff and N. Fourman, Potentiometric Titration (United Sci. Tech. Press, Chem. Theor. Press, 1935), p. 61, 263.

[3] E. Müller and Wertheim, Z. anorg. u. allgem. Chem. 133, 412 (1924).

[4] N. I. Visyagin, Bulletin of the Hallurgy Institute 1939, No. 12, 3.

[5] I. A. Atanasiu and Velculescu, Z. anal. Chem. 90, 1055 (1932).

[6] F. Treadwell and V. Hall, Course of Analytical Chemistry (United Sci. Tech. Press, 1935), Vol. II, Part 2, p. 197, 198.

[7] I. M. Kolthoff and V. A. Stenger, Volumetric Analysis (State Sci. Chem. Lit. Press, 1952), Vol. II, p. 203, 205.

[8] M. L. Thomson, Metallurgia 39, 46 (1948).

[9] I. A. Atanasiu, J. chim. phys. 23, 501 (1926).

[10] A. Shakhkeldian, J. Appl. Chem. 11, 546 (1938).

[11] P. K. Agasyan, Bull. Moscow University, Ser. Phys. Math. and Natural Sci. 1949, No. 1, 2nd communication, 67.

[12] K. Fajans and O. Hassel, Z. Electrochem. 29, 495 (1923).

[13] I. Batchelder and V. Meloche, J. Am. Chem. Soc. 54, 1319 (1932).

[14] A. N. Frumkin, Ber. 60, 1816 (1927).

[15] I. V. Tananaev and N. I. Mirianashvili, J. Appl. Chem. 10, 2088 (1937).

[16] A. A. Medvedovsky, Ukrain. Chem. J. 17, 27 (1951).

[17] J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry (1931), Vol. XI, p. 512.

[18] I. N. Putilova, Textbook on the Practice of Colloid Chemistry (State Sci. Tech. Press, 1952), p. 130.

Received November 28, 1954

HIGH-FREQUENCY ARGENTOMETRIC TITRATION

Yu. Yu. Samitov and V. M. Gorokhovsky

The V. I. Lenin Kazan State University

In recent years high frequency conductometric titration (H.F.T.) has been applied to a number of volumetric analytical problems [1], including precipitation methods [2-10].

The work described here had as its object a more detailed study of the possibilities of H.F.T., using a Q-metric apparatus [1], and applying it to argentometric titration of solutions of halides, thiocyanates, and ferricyanides in the concentration range $\sim 10^{-2}$-10^{-5} N. We were also interested in simultaneous determination of several ions, titration in the presence of an indifferent electrolyte, and the possibility of analyzing natural materials.

EXPERIMENTAL

The work was carried out on a high frequency Q-metric apparatus described previously in an article by one of the authors [11]. An electrical C-cell, type (e) was used; this consists of two metallic rings, 30 mm in diameter and 4 mm wide, fixed at a distance of 5 mm from each other on a polystyrene holder. The cell was connected inductively through a coil to the oscillating circuit of an auto-generator. In some cases, in order to increase the sensitivity of the apparatus, the condenser casing (ring) was connected directly to the ends of the induction coil of the oscillating circuit.

The apparatus was allowed to warm up before starting to work in order to establish thermal equilibrium between the generator parts and the surrounding medium. The length of time for which the apparatus is allowed to warm up depends on the individual quality of the generator tubes and the operational temperature, and is normally 20-40 minutes.

During titration, the beaker containing the test solution was placed in the high frequency electric field of the cell and a rough adjustment made of the initial grid current by means of a null galvanometer (GMP $C_1 \sim$ $\sim 10^{-7}$ A/mm). Changes in the constant grid current applied, which occur on addition of reagent, were followed by taking readings of a mirror galvanometer shunted with a universal shunt. During titration the alignment of the titration vessel with respect to the cell electrodes was kept strictly constant. In order to eliminate effects of volume changes on addition of reagent, the amount of solution originally taken was such that the level of the liquid projected beyond the screen surrounding the cell. Silver nitrate was added to the solution being titrated in 0.05-0.1 ml lots from a 1 ml micro buret. During titration the contents of the titration vessel was mixed vigorously with a glass stirrer driven by an electric motor. Readings were taken after the pointer had come to its equilibrium position. On titrating $2.5 \cdot 10^{-3}$-$2.5 \cdot 10^{-4}$ N solutions, equilibrium was reached in a matter of a few seconds; when titrations of $2.5 \cdot 10^{-5}$ N was carried out, however, it was necessary to wait a rather longer time (10-20 seconds).

The following solutions were prepared: $AgNO_3$ solutions 0.1, 0.01 and 0.001 N; KCl, KBr, and KI solutions 0.01, 0.001, and 0.0001 N; NH_4CNS 0.001 and 0.0001 N; $K_3Fe(CN)_6$ 0.003 and 0.0003 N. Potassium chloride and ammonium thiocyanate solutions were prepared from special grade reagents, while the rest were prepared from analytical grade reagents.

2-5 ml of test solution was placed in a beaker to be used for titration and diluted with water to ~ 20 ml. During titration of dilute solutions ($2.5 \cdot 10^{-4}$-$2.5 \cdot 10^{-5}$ N) twice distilled water was used for dilution.

When potassium bromide, potassium iodide, and ammonium thiocyanate solutions were titrated in the concentration range $2.5 \cdot 10^{-2}$–$2.5 \cdot 10^{-4}$ N, V-shaped titration curves were obtained. The end point was found by the intersection of the two branches of the titration curve (Fig. 1, Curve 1). The results obtained are collected in Table 1. The table contains the mean values of the end points from n determinations, as well as the limiting absolute ($\bar{\epsilon}$) and relative (δ) errors, found by mathematical treatment of the results [12]. During titrations of solutions of potassium chloride and ammonium thiocyanate, concentration of silver nitrate was calculated, on the basis of which the concentrations of solutions of potassium bromide, potassium iodide, and potassium ferricyanide were determined (Table 1).

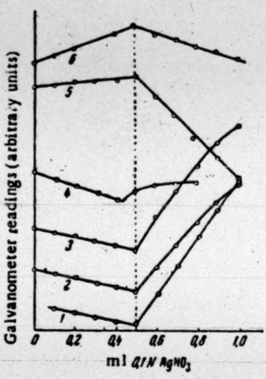


Fig. 1. Titration of 5 ml of 0.01 N KCl on addition of 0.1 N $NaNO_3$; ν = 35.0 megacycles. 1) without $NaNO_3$; 2) 0.5 ml $NaNO_3$; 3) 1 ml $NaNO_3$; 4) 2 ml $NaNO_3$; 5) 5 ml $NaNO_3$; 6) 10 ml $NaNO_3$.

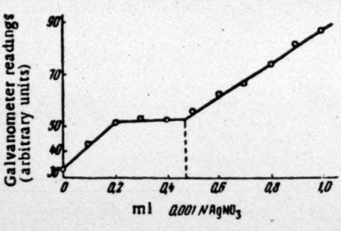


Fig. 2. Titration of 5 ml 0.0001 N KCl + 13 ml H_2O; ν = 35.0 megacycles.

During titration of potassium chloride and potassium ferricyanide solutions with a total concentration of $2.5 \cdot 10^{-5}$ N, a break was observed in the left branch of the titration curve; a curve of this type is shown in Fig. 2. Since a break of this kind only occurs at concentrations which are commensurate with ionic concentrations in a saturated solution of silver chloride (Solubility $\text{Product}_{AgCl} = 1 \cdot 10^{-10}$) and silver ferricyanide (Solubility $\text{Product}_{Ag_3Fe(CN)_6} = 9.8 \cdot 10^{-26}$), it can be treated as follows. At the beginning of titration, on the addition of the first lots of silver nitrate, no precipitate forms, since $[Ag^+] \cdot [Cl^-] <$ Solubility Product_{AgCl}, the increase in conductivity of the solution is the result of uncombined silver ions. On further addition of silver nitrate, the product of the concentrations $[Ag^+] \cdot [Cl^-]$ becomes equal to, or greater than, Solubility Product_{AgCl}, and silver chloride starts to precipitate; this leads to another change in the electroconductivity of the solution and to a break in the left branch of the titration curve. When the equivalence point is reached the electroconductivity starts to grow as a result of the presence of excess silver nitrate ions.

We also titrated potassium chloride in the presence of an indifferent electrolyte ($NaNO_3$). On Fig. 1 are shown the titration curves in this case. Consideration of these curves shows that, on increasing the sodium nitrate concentration to 0.01 N, the right hand branch of the curve curls, while on further increasing the sodium nitrate, an inversion of the points is observed and the titration curve is transformed from a V-shaped to an Λ-shaped curve. An explanation of this peculiarity is given below.

In order to study the effect of excess indifferent electrolyte, and the possibility of simultaneous determination of several ions, experiments were carried out on determination of iodide in the presence of chloride or bromide. Concentrated ammonia was added to the solution to be titrated in order to complex silver chloride and bromide; to increase the total concentration of the solution, sodium nitrate was also added. It was established that a 100% excess of chloride and a 100% excess of bromide, respectively, with respect to iodide, had no effect on the accuracy with which the end point could be determined; this is clearly shown by the results given in Table 2. For ordinary conductometric titration, as Kolthoff has shown [13], even a 50% excess of bromide with respect to iodide leads to an error of 3.6% in determination of the latter.

We used H.F.T. for determining chloride in natural waters. 1-20 ml of water was used for these experiments. Titration curves are V-shaped. Results for the titrations of four samples of natural water of different types are given in Table 3. The method enables small amounts of chloride to be determined rapidly with fair degree of accuracy.

TABLE 1*

$AgNO_3$ concentration	KCl 5 ml 0.01, 0.001 in 0.0001 *N*	NH_4CSN 5 ml 0.001 in 0.0001 *N*	KBr 5 ml	KI 5 ml	$K_4Fe(CN)_6$ 2 ml
0,1 *N*	0.499 ml $(n = 6)$ $C_{AgNO_3} = 0.100 \pm$ ± 0.0001 *N* $\delta = 0.9\%$	—	0,379 ml $(n = 5)$ $C_{KBr} = 0.00758 \pm$ ± 0.00009 *N* $\delta = 1.1\%$	0,492 ml $(n = 5)$ $C_{KI} = 0.00984 \pm$ ± 0.00008 *N* $\delta = 0.7\%$	—
0,01 *N*	0.500 ml $(n = 10)$ $C_{AgNO_3} = 0.0100 \pm$ ± 0.0002 *N* $\delta = 2.3\%$	0.504 ml $(n = 5)$ $C_{AgNO_3} = 0.0099 \pm$ ± 0.0001 *N* $\delta = 1.1\%$	0.391 ml $(n = 5)$ $C_{KBr} = 0.00078 \pm$ ± 0.0002 *N* $\delta = 2.6\%$	0.498 ml $(n = 5)$ $C_{KI} = 0.000996 \pm$ ± 0.000009 *N* $\delta = 0.8\%$	0.600 ml $(n = 5)$ $C_{K_4Fe(CN)_6} = 0.00300 \pm$ ± 0.00007 *N* $\delta = 1.5\%$
0,001 *N*	0.526 ml $(n = 7)$ $C_{AgNO_3} = 0.00095 \pm$ ± 0.00006 *N* $\delta = 6.4\%$	0.512 ml $(n = 7)$ $C_{AgNO_3} = 0.00098 \pm$ ± 0.00005 *N* $\delta = 4.6\%$	0.404 ml $(n = 5)$ $C_{KBr} = 0.000081 \pm$ ± 0.000004 *N* $\delta = 5.3\%$	0.502 ml $(n = 5)$ $C_{KI} = 0.000101 \pm$ ± 0.000003 *N* $\delta = 3.1\%$	0.631 ml $(n = 4)$ $C_{K_4Fe(CN)_6} = 0.000316 \pm$ ± 0.000004 *N* $\delta = 1.0\%$

---

*n – number of determinations.

TABLE 2

Added to 5 ml of 0.01 N KI	—	5 ml 0.01 *N* KCl 0.5 ml 20% NH_4OH	5 ml 0.01 *N* KCl 0,5 ml 20% NH_4OH 5 ml 0.1 *N* $NaNO_3$	2,5 ml 0.01 *N* KBr 2 ml 20% *N* H_4OH 5 ml 0.1 *N* $NaNO_3$	5 ml 0.01 *N* KBr 2 ml 20% *N* H_4OH 5 ml 0.1 *N* $NaNO_3$
0.1 N $AgNO_3$ used in titration, in ml	0.492 —	0.485 0.500	0.495 0.500	0.495 0.495	0.492 —

TABLE 3

Water	Found in g/liter	According to published results(g/l)
Izhevsky	1,13 ± 0,04 $\delta = 3,7\%$	1,12 [14]
River Kazanka	0,0161 ± 0,0001 $\delta = 1,2\%$	—
Kazan water supply	0,0080 ± 0,0001 $\delta = 1,6\%$	—
River Volga (at Kazan)	0,00536 ± 0,00004 $\delta = 1,0\%$	0,00533 [14]

DISCUSSION OF RESULTS

Q-meters are less stable than F-meters; nevertheless, in contrast to the latter, they permit one (at one frequency) to carry out titrations over a wider concentration range, using for this purpose both branches (ascending and descending) of the characteristic curve (Fig. 3,B). In addition, Q-meters are simple in construction and reliable to work with. Fluctuations in the constant grid current applied are observed after warming up, only at high sensitivities of the mirror galvanometer, and are connected with changes in temperature of the tube generator.

H.F.T. is highly sensitive; it is possible to determine 20 γ chloride ion in 20 ml solution (10^{-5} N). Low frequency conductometric measurements, according to Kolthoff's results [13] permits, in limiting cases, titration of 100 ml $2.5 \cdot 10^{-4}$ N solution amounting to 900 γ chloride ion in 100 ml. Calculation of the titration error for normal argentometric titration, when potassium chromate is used as indicator, for chloride concentrations of $2.5 \cdot 10^{-3}$ N shows that it is 1.1% [15], while for lower concentrations calculation shows the impossibility of achieving the accuracy of H.F.T. E.g., for $2.5 \cdot 10^{-4}$ N potassium chloride, titration error is 11%, while for $2.5 \cdot 10^{-5}$ N potassium chloride, titration error is 110%; H.F.T., on the other hand, in the first case gives $\delta = 2.3\%$, and in the second case $\delta = 6.4\%$.

With increasing total ionic concentration of the solution, there is observed, as pointed out above, an inversion of the points on the titration curve (Fig. 1), while at some intermediate concentration of the indifferent electrolyte and a given oscillation frequency, it becomes even impossible to determine the end points (Fig. 1, Curve 4). Following Reilley [16], this characteristic of H.F.T. can be explained as follows.

A study of high frequency conductivity by means of Q-meters with electric type C-cells shows that the curve relating high frequency conductivity to concentration (characteristic curve), passes through a maximum, while in the case of electrical L-cells, it passes through a maximum and a minimum [11].

The characteristic curve of a C-cell is shown on Fig. 3,B. Here, apparatus readings which are proportional to the high frequency conductivity of the cell are plotted along the ordinate, while specific conductivity is plotted along the abscissa. If, during titration, the specific conductivity of the solution changes within such limits that the high frequency conductivity corresponds to the branch of the characteristic curve ascending to the maximum, then, as is evident from Fig. 3,A, we get a V-shaped curve (Fig. 1, Curves 1, 2, and 3). In this case, if during titration the changes in conductivity do not take the working point beyond the limits of the descending branch, we get a Λ-shaped curve (Fig. 1, Curves 5 and 6). Finally, if the conductivity, corresponding to the titration end point, lies on one of the branches of the characteristic curve, while the conductivity of the solution at the beginning and the end of titration, respectively, are on another branch, then we get either a W-shaped or Λ-shaped curve. All the same, these complications in the shape of the titration curve have no effect, as can be seen from Fig. 2, on the accuracy with which the end point is determined. There is one unfavorable case possible; this occurs when the high frequency conductivity at the end point corresponds to points on the characteristic curve near the maximum. This case was realized in one of our experiments (Fig. 1, Curve 4). As can be seen from Fig. 1, the errors in determining the end point are very great in this case. Nevertheless, by addition of an indifferent electrolyte, the working point can be readily shifted to a more favorable part – the descending branch, and the end point accordingly determined with the former accuracy.

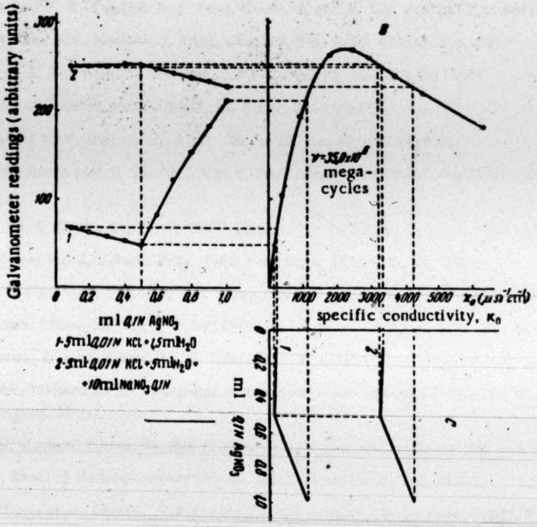


Fig. 3. Relation between low frequency and high frequency titration curves.

Thus, in contrast to low frequency conductometric measurements, excess of indifferent electrolyte in the case of H. F. T., in some cases, proves to be even necessary, since it allows one to bypass the unfavorable part corresponding to the maximum of the characteristic curve and, in fact, increases accuracy of determination of the titration end point.

On should note that on going from low frequencies to higher ones, the position of the maximum on the characteristic curve is displaced regularly to regions of higher concentrations. Concentration C*, which corresponds to the position of the maximum can be calculated beforehand by means of the semi-empirical formula:

$$\lambda C^{*} = 23{,}29\,\frac{D}{\Lambda_0},$$

found by Yu. Samitov [11]; here λ is the wavelength of the generator in cm; D – the dielectric permeability of the solvent; Λ_0 – the limiting conductivity of a uni-univalent electrolyte; C* – the electrolyte concentration corresponding to the maximum.

SUMMARY

1. Using a Q-metric apparatus high frequency titration of chloride, bromide, iodide, thiocyanate, and ferricyanide has been carried out in the concentration range $2.5 \cdot 10^{-3}$-$2.5 \cdot 10^{-5}$ N.

2. The advantages of high frequency titration over low frequency conductometric measurements and normal volumetric methods, respectively, have been demonstrated, particularly for determination of low concentrations.

3. Iodide has been determined in the presence of chloride or bromide, and chloride has also been titrated in the presence of an indifferent electrolyte (sodium nitrate).

4. It has been shown that high frequency titration can be used for analysis of natural materials.

LITERATURE CITED

[1] O. L. Kaptsan and V. A. Teplyakov, J. Anal. Chem. 8, No. 3, 131 (1953) (T.p. 151).*

[2] V. A. Zarinsky and D. I. Koshkin, J. Anal. Chem. 9, No. 1, 29 (1954) (T.p. 29).*

[3] K. Anderson, E. S. Bettis and D. Revinson, Anal. Chem. 22, No. 6, 743 (1950).

[4] J. L. Hall and J. A. Gibson, Anal. Chem. 23, No. 7, 966 (1951).

[5] W. J. Blaedel and H. V. Malmstadt, Anal. Chem. 22, No. 11, 1413 (1950).

[6] H. Goto, T. Hirayama and S. Suzuki, J. Chem. Soc. Japan, Pure Chem. Sect. 74, 216 (1953); C.A. 47, 8578.

[7] O. L. Milner, Anal. Chem. 24, No. 8, 1247 (1952).

[8] S. Musha, Science Repts. Tohoku Univ. 1952, Ser. A., 4, 575; C.A. 47, 9847.

[9] H. Goto and T. Hirayama, J. Chem. Soc. Japan, Pure Chem. Sect. 73, 656 (1952); C.A. 47, 4785.

[10] G. S. Bien, Anal. Chem. 26, No. 5, 909 (1954).

[11] Yu. Yu. Samitov, J. Anal. Chem. 11, 2, 149 (1956) (T.p. 153).*

[12] K. P. Yakovlev, Mathematical Treatment of Results of Measurements (State Tech. and Theor. Lit. Press, Moscow-Leningrad, 1950).

[13] J. M. Kolthoff, Z. anal. Chem. 61, 229 (1922).

[14] O. A. Alekin, Bases of Hydrochemistry (Hydro. Geol. Press, Leningrad, 1953).

[15] I. M. Kolthoff and V. A. Stenger, Volumetric Analysis (State Chem. Press, 1952), Vol. II.

[16] C. N. Reilley and W. H. McCurdy, Anal. Chem. 25, No. 1, 86 (1953).

Received December 10, 1954

---

*T.p. = C. B. Translation pagination.

SPECTROGRAPHIC DETERMINATION OF SODIUM AND POTASSIUM IN SILICATE ROCKS

E. E. Vainshtein and V. V. Korolev

Significant success has been achieved recently in the use of spectrographic methods for analyzing silicate rocks [1,3]. In 1954 a monograph by Ahrens was published which was devoted to this question [4].

In a previous article we have described a method for the quantitative determination of the main components of silicate rocks [5]. In the present article a description is given of a method for determining sodium and potassium quantitatively in clays and granitoids.

The chemical methods normally used for silicate analysis are known to be very tedious; these methods require, on the part of the analyst, considerable experience and very accurate work. As to the accuracy of these determinations, one can refer to results published recently [6]; these were obtained by comparing the analytical results obtained on the same samples by 34 chemists in 25 laboratories throughout the world; the mean relative error for the determination of individual elements varied within the limits 4-6%.

Apart from the fact that spectrographic methods for determination of sodium and potassium in silicate rocks apparently are not less accurate than chemical methods, they simplify and speed up analysis considerably, thereby opening up new possibilities for the solution of various geochemical and petrochemical problems.

Analytical Procedure

The sodium and potassium contents of clays and granitoids of different age and origin change within fairly wide limits; thus, clays contain 0.5-7% K_2O and 0.5-4% Na_2O, while granitoids may contain up to 10-12% K_2O and Na_2O.

From a methodological point of view, it is convenient to distinguish two types of determinations: analysis of rocks with a relatively small content of the alkali metals, and analysis of silicates which are rich in these elements. In the latter case, one must take into account difficulties connected with the possibility of self-absorption of the analytical lines of the elements, and of errors connected with photometric measurements of lines with high intensity. For the analysis of such materials the method involving the width of the spectral line recommends itself.

a) Analysis of rocks containing a relatively small amount of the alkali metals (less than 6-8%). During determination of alkali metals in rocks, soils, and other materials, in order to cut down the effect of the bulk composition of the test material on the analytical results, it is often preferable to work with solutions or melts. If this technique is used, then one may either partially or wholly lose the advantages inherent in the spectrographic method, viz. speed and simplicity. It is more convenient, from our point of view, to use the dilution method, which we have already used earlier for the analysis of clays, for determining the main components [5]. In the course of the present work, we have used as diluent and stabilizing agents: lithium carbonate, cupric oxide, and graphite powder; during checks on their purity it was established that they did not contain more than $5 \cdot 10^{-3}$% Na and K. Lithium was the reference element.

Selection of the optimum ratio of the components in the mixture was carried out experimentally. In practice we settled for a ratio, in parts by weight of sample, Li_2CO_3, CuO, and graphite powder in a mixture of 1:0.5:1:1.5 (100 mg sample + 50 mg Li_2CO_3 + 100 mg CuO + 150 mg graphite powder). Before an analysis the

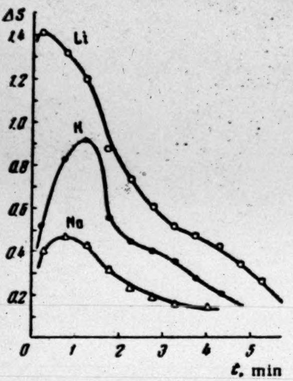


Fig. 1. Relation between blackening of analytical lines of K, Na, and Li, and the length of time for which the arc is burning, during evaporation of these elements from clay.

sample aliquot was dried for 1 hour at 110-115° to remove water. After this the weighed amounts of components were carefully ground in an agate mortar and kept in a bottle with a ground glass stopper. 30 mg of test sample was placed in the crater (diameter 3.5 mm and depth 4 mm) of the lower carbon electrode of an A.C. arc. A spectrographically pure carbon rod ground to a cone with a diameter of 2 mm, served as the upper electrode. The spectra were excited by means of an A.C. arc (Sventitsky type). Current strength – 5 amp. In order to prevent spurting of test material, it was found experimentally that it is best to moisten it before arcing with two drops of twice-distilled water and carefully drying it. Analyses were made, using the lines 7664.9 and 7696.98 A for potassium, and 8194.81 and 8183.27 A for sodium.

The reference line of lithium used was 8126.5 A. Spectra were photographed with an ISP-51 spectrograph which had a camera with a focal length of 270 mm. Slit width was 20 μ; it was illuminated by means of a three-lens condenser. The central part of the arc was projected on the slit. A two-stage attenuator was fitted in front of the spectrograph slit for convenience in carrying out photometric measurements on the spectra. Spectra were registered on "Infrachrome-840" plates with a sensitivity of 40 units H and D; the developer used was D-19. In order to choose optimum exposure conditions, the dynamics of the passage of Na, K, and Li into the arc were studied. The curves relating blackening of the lines of these elements on the spectrogram (with respect to the background) to the time of burning of the arc, are shown on Fig. 1; they show that the optimum exposure time is 2.5 minutes. During this time practically complete evaporation of both the test elements and the reference element occurs.

In constructing calibration curves for determining Na and K in silicates, we used a group of samples[*] of clays and granitoids analyzed accurately by chemical methods, containing from 0.35 to 6% of Na and K. Standards containing higher contents of the alkali elements were prepared synthetically on the basis of the clay with the highest content of these elements (for more details see below). Calibration curves were constructed within the coordinates ΔS, logarithm C, where ΔS is the difference in blackening of the corresponding analytical lines of sodium or potassium and the reference lines. A typical series of graphs is shown in Fig. 2. As can be seen from these curves, on changing the Na and K contents from 0.5 to 8%, they retain their linear form. At higher concentrations of these elements in the rocks, the graphs curve. As checks showed, the mean arithmetical error for a determination, calculated from ten parallel analyses proved to be of the order of 4-5%.

b) Analysis of silicates with high contents of the alkali metals (over 8%). The procedure described above is not applicable to silicates containing more than 8% of Na and K. At higher contents of these elements, the calibration curves constructed in the coordinates ΔS, lose their straight line character. As experiment showed, for analysis of silicates with high contents of the alkali elements (from six to a few tens percent), the spectral line width method can be used with great success. This method, which was first proposed by Gerlach and Rolwagen [7] and which has been subsequently used in a number of papers on spectrographic analysis [8-10], is widely used at present in x-ray spectroscopy [11-12]. When this method is used, it is not the blackening of the analytical line that is chosen for characterizing the content of the test element, but the width of this line, measured at the height of the peak of the reference line, when the intensity of the latter is less than the intensity of the test element line.

---

[*] Chemical analyses of the standard samples of clay were carried out in the Geochemical Laboratory of the Geochemical Institute (A.B. Ronov). Granitoid samples were kindly placed at our disposal by N. I. Khitarov and M. K. Belshterly; we should like to thank them for these samples.

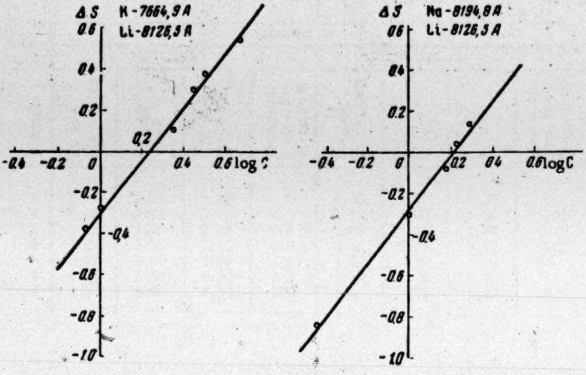


Fig. 2. Calibration curves for detemination of Na and K in clays.

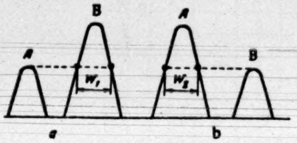


Fig. 3. Two possible variants when the spectral line width method is used (A – lithium line; B – line of the test alkali element): Variant a – the line of the reference element is "projected" on the analytical line of the test element; Variant b – the analytical line of the test element is "projected" on the reference element line.

If the reverse holds (i.e. the intensity ratio is the other way) the line of the test element is "projected" during analysis onto the line of the reference element (Fig. 3, a and b). In both instances, analysis is carried out by means of an experimentally established relation between the width of one of the lines at different parts of it (w) and the logarithm of the concentration of the test element; this relation is established under the conditions chosen for the experiment (width and shape of the spectrograph slit, excitation conditions). When this is done, it can be shown that the parameters of the calibration curve obtained in this way should depend very little on the conditions of development of the photographic plates.

A drawback of the method, when it is used in optical spectral analysis, is the relation between line width and spectra excitation conditions, the size and form of the spectrograph slit, and the difficulty of using it in practice when working with very narrow spectral lines. All these factors may have an unfavorable effect on the accuracy of determination when this method is used. For the spectral lines of Na, K, and Li, arranged in the spectral region from 7000 to 8300 A, the latter difficulty however does not apply, since the width of these lines is fairly big and can be readily measured with satisfactory accuracy. There is no need to construct all the contour of the spectral line of the element for this purpose. The line width at any cross section can be determined as a difference of two readings (counted off on the drum of the micrometric screw of the photometer), corresponding to two opposite points on the line, the blackening of which are equal to the blackening of the reference line. Results of measurement can be conveniently expressed in Angstroms, to do which, the width of the line measured on the microphotometer in millimeters, can be multipled by the dispersion of the apparatus in the given spectral region.

In order to construct calibration curves whereby it is possible to analyze silicates by means of the spectral line width method, standard samples were used which had known contents of Na and K, ranging from a few percent to 30% (determined by chemical methods). Analysis was carried out under conditions similar to those described above. Before analysis, the test was mixed in definite proportions with Li_2CO_3, CuO, and graphite powder.

TABLE 1

Comparison of Results of Spectrographic Analysis of Clays by Two Methods

Samples	Content in %							
	K_2O				Na_2O			
	By line blackening	By line width	Mean	Deviation from the mean in %	By line blackening	By line width	Mean	Deviation from the mean in %
1	1.12	1.27	1.19	6.0	0.30	0.30	0.30	0
2	3.70	3.71	3.70	0	1.12	1.03	1.07	3.8
3	2.25	2.20	2.22	0.5	1.67	1.60	1.63	1.80
4	3.67	3.22	3.45	6.6	0.58	0.46	0 52	1.2
5	3.18	2.96	3.07	3.6	1.10	0.90	1.00	10
6	1.58	1.82	1.70	1.7	1.10	1.23	1.16	5
7	1.86	2.00	1.93	3.6	1.9	1.76	1.83	3.8

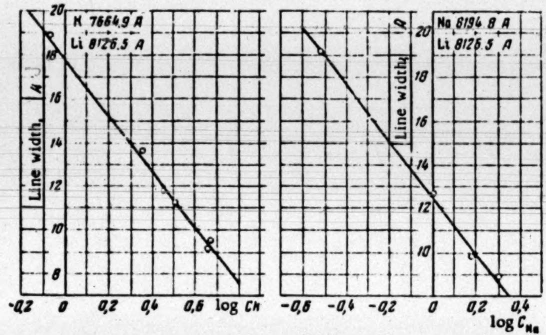


Fig. 4. Calibration curves for determining alkali metals in clays using the spectral line width method (Variant a, Fig. 3).

For analysis of clays and granitoids with a relatively low content of the alkali metals (from 6 to 8) the content of Li_2CO_3 amounted to 14.5% of the weight of the mixture, and analysis was carried out according to the scheme represented graphically on Fig. 3b. The analytical lines of Na and K were "projected" on the more intense Li line. Results of determinations carried out by means of the spectral line width method were compared with those obtained by the normal method; they proved to be in satisfactory agreement with each other (Table 1).

For higher contents of the alkali metals in a test sample, it was found more convenient to decrease the amount of Li in admixture with the other components to 4.3% (15 mg Li_2CO_3 to 365 mg mixture) and to measure the line width in accordance with the variant shown on Fig.3, a. Calibration curves for determining Na and K, obtained in both cases, are shown on Figs. 4 and 5. On the second of these figures for comparison, are shown the normal calibration curves in the coordinates ΔS, logarithm C, constructed for the same concentration ranges of Na and K in a rock. Comparison of both curves emphasizes the advantages of the spectral line width method for analysis of silicates rich in alkali metals. Checks showed that the mean arithmetic error for determination of an alkali metal by means of the spectral line width method varied with the limits 4-6%.

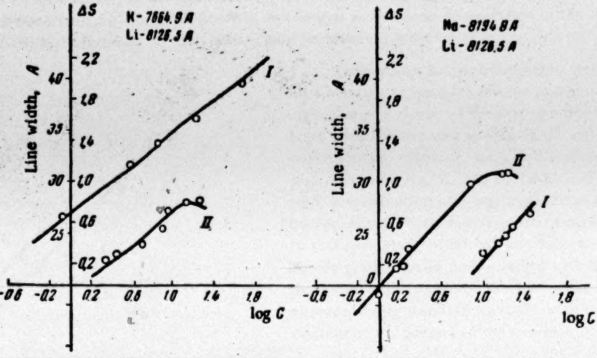


Fig. 5. Comparison of calibration curves for determining Na and K in silicates by two methods:
I) Spectral line width method (Variant b, Fig. 3); II) blackening method.

Relation Between Experimental Results and the Gross Composition of the Rocks and Content of Alkali Metals

In order to study the effect of the gross composition of the test samples (on the results of determination) and the mutual effect of the test elements on one another, we used silicates with varying contents of the major components – Si, Al, Fe, Ca, and Mg, and also synthetically prepared samples with Na and K contents varying over a wide range. In order to prepare the latter, various amounts of Na and K as the sulfate and carbonates were added to a granite sample of known alkali metal content. Rock composition varied within the following limits: SiO_2 from 25 to 72%; Al_2O_3 from 2.5 to 15%; Fe_2O_3 from 1 to 5.5%; CaO from 0.5 to 40%; and MgO from 1.5 to 8.5%. The Na and K contents of standard mixtures varied from 0.5 to 12%. The following were

TABLE 2

Comparison of Results of Spectrographic and Chemical Analysis of Alkali Metals in Certain Silicates

Samples	Clays				Granitoids			
	K_2O		Na_2O		K_2O		Na_2O	
	By chemical analysis in %	By spectroscopic analysis	By chemical analysis in %	By spectroscopic analysis	By chemical analysis in %	By spectroscopic analysis	By chemical analysis in %	By spectroscopic analysis
1	5.27	5.62	0.18	0.22	4.01	4.46	2.01	3.02
2	4.70	4 47	0.25	0.26	4.66	4.62	2.63	2.75
3	4.08	4 36	0.32	0.34	4.81	4.94	2 92	3.16
4	3.98	3.67	0.63	0 58	2.59	3.16	2 65	2.92
5	3 68	3.71	0.92	1.10	3 33	3.10	2.94	2.76
6	2.50	2.25	1.58	1.67	2.39	2.90	3.67	3.01
7	2.42	2.50	1.29	1.23	1.99	2.27	4.02	3.88
8	1.00	1 12	0 35	0 30	4.95	4.90	3.32	3.43
0	1.74	1.58	0.68	0.76	4.67	4.52	3.60	3.32
10	1.23	1.09	0.68	0.79	3 42	3.40	4.26	4.10

studied: the character of the passage of elements into the arc and the behavior of the calibration curves. It was shown that the form and position of the curves characterizing the dynamics of the passage of the alkali metals into the arc, as well as the position of the calibration curves, and the degree of agreement between chemical and spectrographic determinations, are not dependent on changes in the gross composition of the test silicates. No mutual effect of the test elements on each other could be observed either.

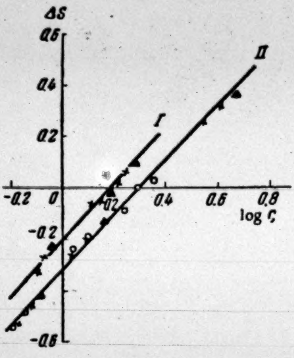


Fig. 6. Calibration curves for determining Na (I) and K (II) in silicates with varying contents of one of the alkali metals: Δ – relates to the original test sample; X – relates to the original sample to which Na and K carbonates have been added; O – relates to the original sample to which Na and K sulfates have been added.

Calibration curves constructed on the basis of results relating to samples of clay and to standards with high contents of one of the test elements, which had been added to the test sample as the carbonate of the corresponding element, remained unchanged. Evaporation curves for Na, K, and Li, both from the rock and from a standard containing, in addition to clay, the carbonate of the alkali metal, were completely identical in this case also. What has just been said is illustrated by the graphs shown on Fig. 6, on which, in addition to the points relating to the original rock, are plotted points characterizing standard mixtures with sharply differing content of the second of the two test alkali elements.

It should be noted, however, that the independence of the results of quantitative determination of one of the alkali metals in the silicate, on the presence of the second element, noted above, is destroyed in the case of Na, if during preparation of standards with a high potassium content, the latter is added as the sulfate to the mixture. The calibration curve constructed using such a standard, although parallel to the original straight line suitable for analyzing clays, is however displaced to the side of high blackenings of the Na analytical lines. The evaporation curve of the element also changes in this case. Without delving, in the present article, into the reasons which determine this characteristic behavior of sulfate as compared to carbonate, we shall merely point out that this fact is in good agreement with observations made previously [13], during analysis of soils and mineral for their contents of certain alkali metals.

Comparisons of the Results of Spectrographic and Chemical Analyses

In order to check on the reliability of the method described above for quantitative spectrographic determination of alkali metals in silicates, we used it for analyzing a large number of clays and granitoids in which the contents of the alkali metals were determined in parallel by chemical methods. Agreement between the results of spectrographic and chemical analyses proved to be completely satisfactory. Results obtained by both methods differed from each other on an average by not more than 7-9%. Table 2 contains some results which exemplify the extent of the agreement between results of spectrographic and chemical analyses.

In conclusion we should like to thank V. P. Avramova who took part in the experimental side of the work.

SUMMARY

1. Two spectrographic methods are described which are suitable for determining sodium and potassium in ilicates at contents of the alkali metals ranging from 0.5 to a few tens percent. The mean arithmetical error for spectrographic determination of sodium in rocks is 4-5%, and for potassium 5-6%.

2. On observing the conditions described for carrying out the analysis, changes over wide limits in the gross composition of test samples have practically no effect on the results of quantitative determination. The elements were found to have no observable mutual effect on each other's determination.

3. The methods developed have been used for analyzing clays and granitoids of different origins and geological age. Comparision of the results of spectrographic and chemical analysis of the alkali metals in the same samples, showed that they were in good agreement (within the limits 7-9%) with each other.

LITERATURE CITED

[1] A. J. Kvalheim, J. Opt. Soc. Amer. 37, 585 (1947).

[2] D. N. Ivanov, Soil Science 1953, 1, 61.

[3] C. Anderson, Anal. Chem. 26, 1369 (1954).

[4] L. Ahrens, Quantitative Spectrochemical Analysis of Silicates (London, 1954).

[5] E. E. Vainshtein, T. F. Borovik-Romanova and V. V. Korolev, J. Anal. Chem. 10, 158 (1955) (T.p. 147).*

[6] H. W. Bairbairn, W. G. Schlicht, R. E. Stevens, W. H. Dennen, L. H. Ahrens and F. Chayes, U. S. Geol. Survey, Bulletin No. 980.

[7] Gerlach and Rollwagen, Metallwirtschaft 16, 1083 (1937).

[8] P. Coneur, Met. Soc. Rev. Science, Liege 5, 1 (1942).

[9] B. Ross, Analyst 76, 903 (1954).

[10] T. K. Aidarov and T. K. Massilon, Technical Information Bulletin 57, 630 (1954).

[11] I. B. Borovsky, Factory Lab. 11, 1935 (1948).

[12] E. E. Vainshtein, I. D. Shevaleevsky, and M. M. Kakhana, J. Anal. Chem. 7, 363 (1952) (T.p. 403).*

[13] S. A. Borovik and T. F. Borovik-Romanova, J. Anal. Chem. 1, 25 (1946).

Received December 19, 1955

---

*T.p. = C. B. Translation pagination.

BLANK
PAGE

BRIEF COMMUNICATIONS

AN IMPROVED METHOD OF INTRODUCING TEST SAMPLES INTO THE ARC FLAME WHEN WORKING WITH AN ACTIVATED A. C. ARC

T. F. Borovik-Romanova

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry
Acad. Sci. USSR, Moscow

During spectrographic analysis of mineral raw materials, particularly of alumino-silicates, when working with an arc struck between carbon electrodes, formation of beads which are spherical in shape is often observed; they are not completely evaporated and at the end of the exposure time they drop off the electrode. These spherical beads differ in size from sample to sample and may affect the analytical results. This phenomenon is particularly marked when the PS-39 generator with an activated A.C. arc operating at current strength from 6 to 8 amperes is used. In this case, the electrode temperature is lower than with a D.C. arc (~ 2500°), which leads to a slower evaporation of test sample. Thus 0.06 g of albite evaporates in the course of 9 minutes from the crater of an electrode in an activated A.C. arc, and at the end of the ninth or the beginning of the tenth minute the spherical bead remaining drops off. When this weight of albite is taken, viz. 0.06 g, the weight of the spherical bead remaining amounts to 0.015 g; the same is true of feldspar; it is somewhat less in the case of granite samples.

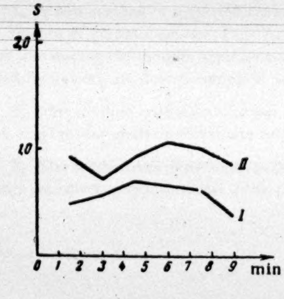


Fig. 1. Evaporation curves for lithium from albite (Curve I) and feldspar (Curve II) in an activated A.C. arc.

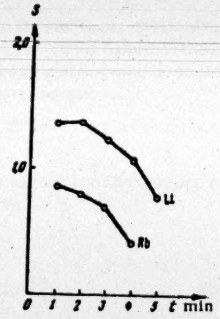


Fig. 2. Evaporation curves for Rb and Li from feldspar when graphite power is placed on the bottom of the electrode before sprinkling on the test sample.

Spectrograms taken on a moving plate showed that a large part of the elements, including the rare alkali metals, remains to the end of exposure, and their lines can still be detected when the spherical bead which dropped off during the first exposure is evaporated a second time from a new electrode. On Fig. 1 are shown evaporation curves for lithium from albite (Curve I) and feldspar (II). Only the lines for lead and copper disappeared after the fourth minute.

These facts compelled us to change the mode of introducing test materials into the arc flame. Graphite powder in an amount 1.5-2 times as much as that of the test sample is placed in the electrode crater (before sprinkling on the sample). Thus, for a test sample weighing 0.015 g, one takes 0.03 g of graphite powder for an electrode crater 4 mm deep and 3.5 mm diameter. The graphite powder is tamped down with a glass or metal rod. A small amount of graphite powder is sprinkled on top of the test sample so as to avoid spattering of test sample when the arc is lit. To increase sensitivity both sample weight and weight of graphite powder can be proportionately increased.

When graphite powder is put on the bottom of the electrode in this way, the sample evaporated evenly and completely. A sample weighing 0.015 g evaporated in 5 minutes when the current was 7 amperes. Evaporation curves for rubidium and lithium from feldspar are shown on Fig. 2. Results obtained when this technique is employed are fairly reproducible and even better reproducibility can be achieved by using an electrode made up according to Scribner consisting of a cap and a base. The cap was 12 mm long and the crater in the upper part had a depth of 4 mm and a diameter of 3.5 mm; test sample was placed in the crater; in the lower part of the cap was a crater by means of which the cap was fitted on to the base which was in the form of a carbon rod constricted at its end.

The method indicated has been used for a long time for spectrographic determination of lithium, rubidium, and cesium. Instead of a reference element the background lying close to the lines of the test elements was used. The relative error (mean arithmetical) was ±6-10%.

This technique of introducing test samples into the arc flame enables one to avoid sputtering and scattering of the sample, and analysis of samples of minerals can be carried out with reasonable accuracy on a PS-39 generator at currents of 6-8 amperes. This technique of putting the graphite powder at the bottom of the electrode crater has still one further advantage, viz. sensitivity does not drop as is the case when the graphite powder is mixed in with the sample.

SUMMARY

1. A new method is suggested for introducing test samples into the arc flame; this involves placing a large amount of graphite powder (1.5-2 times the amount of test sample) on the bottom of the electrode crater before introducing the sample itself into the crater; this prevents sputtering of test sample, lessens the chances of bead formation, and favors complete and even evaporation of the test sample.

2. This method enables one to use an activated A.C. arc (PS-39 generator) operating at current strengths of 6-8 amperes for analysis of silicate rocks.

3. The method has been used for the analysis of silicate rocks and minerals for lithium, rubidium, and cesium; the relative experimental error (mean arithmetical) is ±6-8%.

Received April 19, 1955

EXCITATION OF CRYSTAL FORMATION BY FRICTION DURING ANALYTICAL REACTIONS

F. M. Kutsakov

The V. I. Lenin Kharkov Polytechnical Institute

Friction very often favors crystal formation during chemical reactions. Many research workers [1-3], have studied this complex phenomenon. The most widespread explanation which reduces to the formation during friction, of grains of rubbing materials which act as centers of crystallization, is however not enough [1,4].

Existing methods [3], and the little available apparatus are not sufficient for solving many problems.

In the course of the work described here, which was mainly carried out with small volumes of solutions, some new experimental and methodological possibilities were discovered in the field of excitation of crystal formation by friction.

EXPERIMENTAL

The phenomena of crystal formation described here were initially established during formation of precipitates of $KHC_4H_4O_6$, $Na_2H_2Sb_2O_7$, and $MgNH_4PO_4$; they were subsequently reproduced during preparation of precipitates of $K_2Ba[Fe(CN)_6] \cdot 5H_2O$; $Co[Hg(SCN)_4]$; $Pb[Hg(SCN)_4]$; CH_3COOAg; $AgBrO_3$, BaS_2O_3; Ag_2SO_4, the formation of which is favored by friction. The precipitates were prepared under normal conditions of macro analysis in test tubes and by the method of microcrystalloscopy on plates [4]. During these experiments, the sequence in which the respective solutions were placed on the plates, the material and the shape of the rods, the method used for applying friction, and also the material from which the plates were made (glass, platinum, paraffin, and cellophane) were all varied. The rods used for applying friction were made of glass, porcelain, platinum, steel, copper, aluminum, wood, paraffin, paper, and bird feathers, respectively. The pressure of the rods on the plates and the rate with which they were moved in the solution were evaluated qualitatively.

General observations are made below.

I. Series of tests. Friction lines of different widths and depths were first made on the plates by means of a sharp porcelain rod; the solutions were then added in a certain sequence. Well regulated crystal formation was not observed along the friction lines; preliminary marking of the object glass with other rods did not lead to well regulated crystal formation either.

II. Series of tests. The reagents which give rise to the precipitates were first placed on the plates, and then the plates were etched through the solution, using rods held with varying pressures and moved at different rates. In these cases there was observed regular accumulations of crystals along the tracks made by the rods, on the background of the transparent solution, or in the field of evenly distributed crystals (Figs. 1-4).

III. Series of tests. The plates were marked through the solution, as in Series II, in some cases using glass rods, and in others with a glass capillary so that during the time that the capillary was moved about, the solution was drawn inside the capillary. When this was done it was observed that the crystals along the friction lines were more developed in the case of the glass rods.

IV. Series of tests. Relation between crystal formation and pressure of rod on plate was studied in detail when a platinum rod was used for rubbing the solution against the plate, no observable differences between

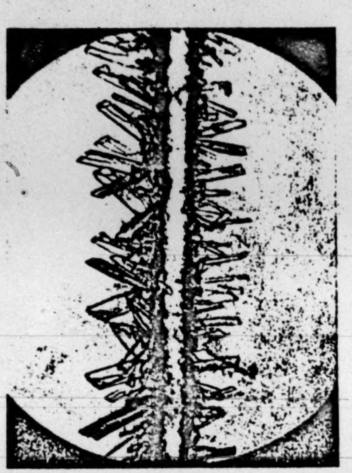


Fig. 1. $KHC_4H_4O_6$

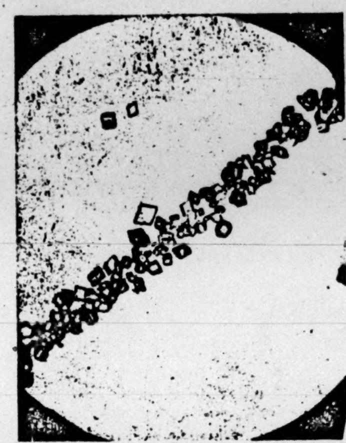


Fig. 2. $K_2Ba[Fe(CN)_6] \cdot 5H_2O$

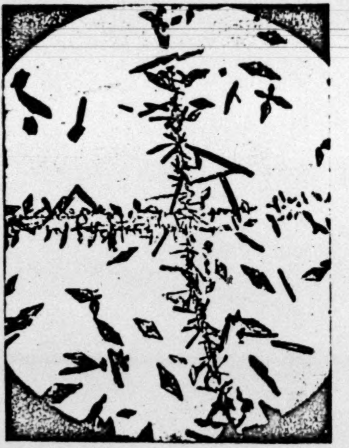


Fig. 3. Ag_2SO_4

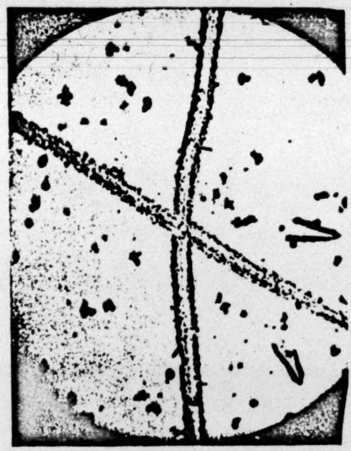


Fig. 4. $AgBrO_3$

Figs. 1-4. Regular accumulation of crystals on the background of the transparent solution or in the field of uniformly dispersed crystals.

friction lines could be found in all cases. A totally different picture was obtained when the rate at which the rod was moved was changed: slow movement of the rod led to the appearance of a few large crystals along friction lines, while rapid motion of the rod led to copious formation of small crystals, which with time grew amongst each other in a clearly defined fashion along the direction of the friction lines.

V. Series of tests. Formation of crystals changes very considerably with change in reagent concentration; it decreases with dilution.

TABLE

Dilution	Induction period in seconds	Development period of marks in seconds
1 : 1	0	2
1 : 10	0	5
1 : 20	0	15—25
1 : 30	0	35—55
1 : 30	20	35
1 : 30	55	5—35
1 : 40	60	120
1 : 50	60	240 barely perceptible
1 : 50	120	180 perceptible

During these same experiments it was found that considerable improvement in crystal formation along the friction lines occurs on increasing the length of time between pouring together of reagents and making the friction lines. The duration of this period can be called the induction period of the friction line. The length of the time which elapses between stirring of the solution with a rod and appearance of an observable precipitate can be called the development time of the friction line.

Results of this series of tests are given in the table.

Rates of crystal formation along the friction lines, for different materials which were treated in the same way, were found to differ. Thus, for $KHC_4H_4O_6$ an appreciable precipitate was obtained after 2 seconds; under identical conditions, a precipitate of $Na_2H_2Sb_2O_7$ formed only after 300 seconds.

DISCUSSION OF RESULTS

From a comparison of the results of all these tests it follows that during excitation of crystal formation in supersaturated solutions by friction, of fundamental importance is the disturbance of the layer of solution near the wall of the containing vessel on the boundary of separation of the two phases [2], and not the small particles of rubbing material.

The growth of crystals along the friction line starts on the surface of the plate and containing vessel, and gradually develops in the volume in accordance with the law of geometric selection. Fine crystals often dissolve completely in the gaps in growing crystals.

Crystal concretions, developing along a friction line, split off from the substrate. In order to clarify the position with regard to crystal formation by friction, it is expedient to distinguish between the period of induction and the period of development of the friction line; this has been done for the first time in the present article. For an equal induction time, the time of development of the friction line may serve, to some extent, as a criterion for the quantitative determination of the content of crystallizable material in solution.

SUMMARY

Excitation of crystal formation by friction has been studied under normal conditions obtaining in macro and micro analysis, by rubbing the solution against the containing walls with rods made of different materials.

It has been found that the main reason for formation of crystals along friction lines is the disturbance of the layer of solution at the containing walls.

It has been shown that there is a connection between concentration of crystallizable material in solution, the induction period of the friction line, and the development period of the latter as well.

LITERATURE CITED

[1] A. V. Shubnikov, How Crystals Grow (Acad. Sci. USSR Press, 1935).

[2] V. D. Kuznetsov, Crystals and Crystallization (State Chem. Press, Moscow, 1953).

[3] G. Balki, Crystal Growth (Foreign Lit. Press, Moscow, 1954).

[4] I. M. Korenman, Micro-Crystalloscopy (State Chem. Press, Moscow, 1947).

Received November 22, 1954

A QUANTITATIVE METHOD OF DETERMINING ACRYLONITRILE BY MEANS OF SODIUM SULFITE

A. P. Terentyev and S. I. Obtemperanskaya

M. V. Lomonosov Moscow State University

Acrylonitrile $CH_2 = CH \cdot CN$ is being used on an ever increasing scale in industry for the production of synthetic rubber, plastics, etc.; accordingly, development of analytical methods for this material is of considerable practical interest.

TABLE

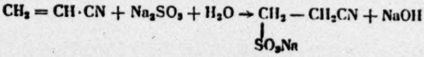
Sample weight in g	0.1 N HCl used for titration	Duration of reaction	Acrylonitrile found in %
0.0769	14.15	1 hr.	99.94
0.0560	10.80	1 hr.30 min.	100.13
0.0599	10.95	1 hr.30 min.	100.10
0.0667	12.20	2hr.	100.00
0.0840	15.35	2hr.	99.97

Existing methods of analyzing acrylonitrile – spectrophotometric [1], polarographic [2], and spectroscopic (infrared) [3], cannot be used in all cases. The most satisfactory is a method based on interaction of acrylonitrile with dodecyl mercaptan, excess of which is back-titrated with iodine. The accuracy of the method is ± 0.3% [4,5].

A method has also been described [6], which is based on a reaction between acrylonitrile and a solution of an alkali salt of glycocol; excess glycocol is determined gasometrically by Van Slyke's method in a special apparatus. The accuracy of the method is ± 1%.

We have developed a simple method, entirely suitable for factory practice, for quantitative determination of acrylonitrile, which is based on its reaction with sodium sulfite.

In aqueous solutions, acrylonitrile reacts with sodium sulfite according to the equation [7]:



$$CH_2 = CH\cdot CN + Na_2SO_3 + H_2O \rightarrow \underset{SO_3Na}{\underset{|}{CH_2}} - CH_2CN + NaOH$$

The amount of alkali liberated during this reaction is equivalent to the amount of acrylonitrile which has reacted and can be titrated with acid using thymolphthalein as indicator. The accuracy of the method is ± 0.2%. The acrylonitrile was dried over calcium chloride before analysis. Sodium sulfite was used in aqueous solution (~ 0.25 N). Sodium sulfite solution is readily oxidized by air and also readily absorbs carbon dioxide; it should therefore not be kept for long.

Dioxane was used as solvent for acrylonitrile.

The reaction takes ~ 1-1½ hours to go to completion. The reaction was carried out at room temperature; for speeding up the reaction, however, the reaction mixture can be heated in a round bottom flask fitted with a reflux condenser, on a water bath for 30 minutes. The table contains results of determinations carried out on pure acrylonitrile.

Analytical Procedure

0.05-0.08 g of acrylonitrile in a sealed ampoule is introduced into a 100 ml flask (ground glass neck), and 3-5 ml of dioxane (dried and distilled over sodium) added; the ampoule is broken with a glass rod, the rod rinsed with dioxane and 25 ml of 0.25 N sodium sulfite added from a buret. The solution is mixed and allowed to stand for 1-1½ hours, after which the alkali liberated is back-titrated with 0.1 N hydrochloric acid in the presence of 3 drops of thymolphthalein, till the blue color disappears. A reference solution is used for comparison (25 ml of sodium sulfite solution and 3 drops of indicator). 1 ml of 0,1 N hydrochloric acid is equivalent to 0.005306 g acrylonitrile.

SUMMARY

A method has been developed for determination of acrylonitrile, based on its interaction with sodium sulfite. The accuracy of the method is ± 0.2%.

LITERATURE CITED

[1] H. Brieger, F. Rieders and W. A. Hodes, Arch. Ind. Hyg. Occupational Med. 6, 128 (1952); C. A. 46, 11506 (1952).

[2] W. A. Bird and C. H. Hall, Anal. Chem. 24, 586 (1952).

[3] J. D. Sands and G. S. Turner, Anal. Chem. 24, 791 (1952); H. L. Dinsmore and D. C. Smith, Anal. Chem. 20, 19 (1948).

[4] D. W. Bessing, W. P. Tylor, D. M Kurtz and S. A. Harrison, Anal. Chem. 21, 1073 (1949).

[5] G. J. Janz and N. E. Duncan, Anal. Chem. 25, 1410 (1953).

[6] A.P. Terentyev, P. F. Butskus, and V. G. Yashunsky, J. Anal. Chem. 9, 162 (1954) (T.p. 181).*

[7] O. Bayer, Angew. Chem. 61, 229 (1949).

Received September 12, 1955

---

*T.p. = C. B. Translation pagination.

IDENTIFICATION OF SOLID ORGANIC BINARY SYSTEMS BY MEANS OF THE MELTING POINTS OF THE EUTECTICS

M. Kh. Gluzman and V. P. Rubtsova

Kharkov Scientific Research Institute of Pharmaceutical Chemistry

Melting points of eutectics are usually determined by comparing diagrams of state. If the classical method of Kurnakov [1] is used, then in order to compile the diagrams of state it is necessary to use up tens of grams of the very pure components, and also spend considerable time in order to determine the cooling curves of 20 30 mixtures of differing composition. The simplified methods of Hrynakovsky [2], Rheinboldt [3], and Stock [4], enables one to manage with smaller amounts of material; these methods however still require a great deal of time. Kofler's method [5], requires special apparatus. On the basis of observations made by Saratovkin and Savintsev [6], Avakyan and Lashko [7] and others, on contact melting, Gluzman, Gershuns, and Geguzin [8] have constructed an apparatus, by means of which series of determinations of the melting points of eutectics of binary organic systems can be carried out with satisfactory accuracy. We have improved this apparatus, by substituting the ordinary microscope by a stereoscopic one (Models MBS-1 and 2 of Russian make) whereby it is possible to make more accurate observations of contact melting; also, by shifting the coil to the walls of the oil bath so that is cools the oil, not the block, we ensured more uniform heating of the block.

We used the method of contact melting for identifying individual solid organic compounds and binary systems consisting of solid components which do not interact. This type of identification can be used as an additional index for analysis of unknown organic substances, in a similar way to that done in Clark's system, for forensic-chemical and biochemical analysis during studies on alkaloids, glycosides, sterols, and in other cases, where the maximum amount of identification is required with minimum expenditure of test material. The method can also be used for series control of powders, tablets, and similar pharmaceutical products, actually given to patients, since only 1-2 crystals are used up in the analysis and the weight of powder is hardly affected. This method can replace the existing system of selective control in drug stores, under which analysis of selected packaged materials is carried out by analytical control laboratories which, while ensuring that the workers in the drug store are doing their job properly, does not check on the products actually supplied to patients.

We studied the melting points of the eutectics of 26 organic systems (Table 1). Apart from the use of the method described [8], we also determined the melting points of eutectics of binary mixtures, using just a pinch of the mixtures. The melting points of the original materials were checked for the most part in a contact melting apparatus or in a capillary. All melting point temperatures given are corrected values.

From the table it is clear that:

1. During identification of individual crystalline materials, it is possible to determine the melting point of the eutectics of different binary systems, containing the material it is wished to identify as one of the components. It does not matter whether the test component is placed on the plate and then a crystal of the second component placed on top of it, or whether a crystal of the test material is put on top of the melt of the second component.

2. Agreement between the melting points found for the eutectics and published values are fully satisfactory. Normally, they do not differ by more than 1°; the greatest deviation observed was 2°; these deviations evidently depend on the purity of the original components.

TABLE 1

Melting Point of Eutectics of Binary Organic Systems

Component A	Melting point in °C	Component B	Melting point in °C	Melting point of eutectic		Literature reference to eutectic melting point	Eutectic composition (from literature) (mole % A)	Composition of test binary mixture (mole % A)
				published results in °C	Determined during course of this work in °C			
Salol	41.5	Acetanilide	113.8	40.0	40.2; 39.3	[9]	93.8	93.8
Acetanilide	113.8	Benzoic acid	122.1—122.5	76.0	75.9—76.4 75.4—76.2	[9]	57.6	57.6
Acetanilide	113.8	Phenacetin	134.5	80.0	80,5	[9]	79.1	79.1
Salipyrine	91—92	Acetanilide	113.8	64.0	63.5—64.1 63.4—64.4 63.5—64.1	[9]	42.6	43.6 Random composition
Diphenylamine	51—52.5	Acetanilide	113.8	47.0	46.1—46.6 45.0—46.5	[9]	87.6	Random composition
Acetanilide	113.8	Urea	132.5	102.0	102.0—103.2 102.1—102.8	[9]	80.3	Ditto
Menthol	39.2—41	Acetanilide	113.8	35.0	33.9—34.6 33.3—33.9	[9]	85.2	•
Antipyrine	110.2	Urea	132.5	87.0	85.2—86.2 85.7—86.3	[10]	46.0	•
Menthol	39.2—41	Salol	41.5—42	28.5	27.9—26.8 26.3—27.1	[10]	54.8	•
Menthol	39.2—41	Antipyrine	110.2	33 0	32.6—33.0 32.5—33.1	[10]	83.7	•
Diphenylamine	51—52.5	Resorcinol	109.6	51.0	49.2; 49.2	[11]	94.0	•
Resorcinol	109.6	Hydroquinone	172.0	92.0	92.2; 92.0	[11]	77.0	•
Salol	41.5—42	Resorcinol	109.6	38.0	37.8; 37.7	[11]	90.7	•
Resorcinol	109.6	Benzoic acid	121.1—122.5	86.0	85.4; 86.5	[11]		•
Acetanilide	113.8	Hydroquinone	172.0	77.5	75.1—77.1	[9]	60.2	•
Benzoic acid	121.1—122.5	Cinnamic acid	133.8	82.0	81.2—82.3	[12]	57.0	•
Diphenylamine	51.5	Naphthalene	80.0	30.5	30.8; 31.0	[12]	63.6	•
Meta-nitrophenol	94.9—95.1	Picric acid	120.3	71.0	71.5—72.6	[12]	56.9	•
p-Toluidine	41.5	Naphthalene	80 0	31.9	30.4—30 7	[12]	72.5	•
Monochloroacetic acid	60.6	Cinnamic acid	133.8	47.6	46.4; 46.8	[12]	75.0	•
Salol	40.3	Monochloroacetic acid	60.6	26.7	24.6; 25.4	[12]	60.5	•
Naphthalene	80.0	Benzoic acid	122.0	70.0	67.3; 68.3	[12]	67.0	•
Naphthalene	80 0	Phthallic anhydride	131.6	64.9	64.4; 64.9	[12]	73.9	•
Naphthalene	80.0	α-Naphthol	93.5	61.0	59.6—60.3	[12]	60.5	•
Naphthalene	80.0	Camphor	179.0	32.3	32.3—32 8	[12]	42.0	•
α-Naphthylamine	110.8	Camphor	179.0	55.2	55.0	[12]	36 0	•

TABLE 2

Identification of Medicinal Powders by Determining the Melting Points of Their Eutectics

Component A	Melting point in °C	Component B	Melting point in °C	Published results			Composition of test mixtures (mole % A)	Melting point of eutectic in °C as determined in the present instance	
				Reference	Melting point of eutectic in °C	Eutectic composition (mole % A)		In a grain of the mixture	By placing a crystal of one component on top of the melt of the other
Pyramidone	108	Caffeine	234	not detected	—	—	84.4	103.9	104.0
Pyramidone	108	Antipyrine	110.2	ditto	—	—	48.7	78.8—79.8	78 8—79.3
Pyramidone	108	Phenacetin	134—136.5	»	—	—	32.4	81.5	81.2—81.9
Aspirin	133	Phenacetin	134—136.5	»	—	—	50.0	98.6	99.0
Acetanilide	113.8	Aspirin	133	»	—	—	66.7	82 2	82.4—82.8
Antipyrine	110.2	Codeine	155	»	—	—	95.8	91.9—92.7	92.6—92.9
Salol	41.0	Santonin	171.5	»	—	—	85.1	35.1—36.1 34.6—36.4	35.0—36.0
Salol	41.0	Benzonaphthol	109.0	»	—	—	53.6	33.3—34.1 33.4—34.4	33.5
Phenacetin	134—136.5	Caffeine	234	»	—	—	85.9	127.0—127.5 127.2—127.8	127.4
Salipyrine	91	Codeine	155.0	»	—	—	96.6	77.8	77.4
Pyramidone	108.0	Veronal	189—191	»	—	—	48.2	88.0—89.4	89.1
Terpinehydrate	115.0	Codeine	155.0	»	—	—	90.1	91.4—92.4	90.8—91.9
Salol	41.0	Phenacetin	134—136.5	10	40.0	97.6	45.6	38.8—39.2	39.8—40.6
Antipyrine	110.2	Phenacetin	134—136.5	10	75.0	58 8	48.8	75.0—76.0	75.0—76.0
Antipyrine	110.2	Caffeine	232.7	12	103.0	37.0	85.0	105.6	106.4

3. Reproducibility of eutectic melting points does not exceed 1° (Column 6).

4. To determine the melting point of an eutectic, it is not at all essential to have a binary mixture with a composition corresponding to that of the eutectic. We studied the melting points of eutectic binary systems, corresponding in composition to that of the eutectic, and also systems with compositions corresponding to those of pharmaceutical prescriptions, and therefore differing from that of the eutectic by the method described in [8] as well, and in all cases obtained similar results. Consequently, a binary system of any composition can be identified by observing the melting point of the eutectic of a grain of this mixture (Columns 8-9).

5. The rate of temperature rise near the melting point should be 1° per minute; the time taken to determine the melting point of a eutectic is 10-25 minutes, while for very low melting eutectics it takes 4-6 minutes.

Since it has been demonstrated that the melting points of binary systems agree with the melting points as determined by the contact method, then this method can be used for identifying binary systems of any composition, e.g. medicinal powders. Table 2 contains the results obtained for the melting points of grains of 15 powders. These temperatures are in good agreement with published results; when no published results were available we checked them with melting points determined by placing one crystal of one component on top of a melt of the other component.

SUMMARY

1. A method is suggested for identifying individual solid materials and solid binary organic systems by determination of the melting points of the eutectics by the method of contact melting.

2. It has been shown that it is possible by means of this method to identify binary systems at any ratio of their components.

3. The method requires minimum amounts of materials.

LITERATURE CITED

[1] V. Ya. Anosov and S. A. Pogodin, Basic Principles of Physico-Chemical Analysis (Acad. Sci. USSR Press, Moscow-Leningrad, 1947).

[2] K. Hrynakowski, Z. physik. Chem. A, 171, 101 (1934).

[3] H. Rheinboldt, J. prakt. Chem. 111, 242 (1925), 112, 187 (1926); 113, 199 (1926).

[4] A. Stock, Ber. 42, 2059 (1909).

[5] L. Kofler, Mikroskopische Methoden in der Mikrochemie (E. Haim, Wien and Leipzig, 1936); C. A. 1952, 1, 414; Pharmazie 8, 301 (1953).

[6] D. D. Saratovkin and P. A. Savintsev, Proc. Acad. Sci. USSR 80, 4, 631 (1951); 33, 4, 303 (1941).

[7] S. V. Avakyan and N. F. Lashko, Proc. Acad. Sci. USSR 65, 1, 29 (1949).

[8] M. Kh. Gluzman, A. L. Gershuns, and Ya. E. Geguzin, J. Appl. Chem. 26, 1223 (1953) (T.p. 1167).*

[9] K. Hrynakowski and F. Adamanis, Rozniki Chem. 13, 488-53 (1933); C.A 1933, 11, 2935.

[10] K. Hrynakowski and F. Adamanis, Bull. soc. chim. France [4], 53, 1168-75 (1933).

[11] K. Hrynakowski and F. Adamanis, Rozniki Chem. 14, 189 (1934); C.A. 1934, 11, 2490.

[12] Reference Book on Physical, Chemical and Technical Values, Vol. IV.

Received January 4, 1955

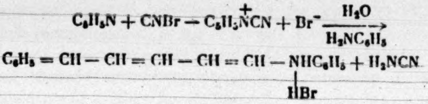
---

*T.p. = C. B. Translation pagination.

COLORIMETRIC DETERMINATION OF PYRIDINE IN AIR

M. I. Tarenko
Institute of Labor Hygiene and Professional Diseases,
Ministry of Health, Georgian SSR

A number of methods are known for detecting and determining pyridine [1-6]. The methods most often used are those based on color reactions connected with formation of intensely colored glutaconic aldehyde. The most intense color is obtained when glutaconic aldehyde is further condensed with aromatic amines. When this is done, the opening up of the pyridene ring can be realized by using various chemical agents [1,5-8]. Nevertheless, the basis for quantitative methods of determining pyridine in air is a very sensitive color reaction in which cyanogen bromide and aniline are used; this reaction proceeds as follows:



$$C_5H_5N + CNBr \rightarrow C_5H_5\overset{+}{N}CN + Br^- \xrightarrow[H_2NC_6H_5]{H_2O}$$
$$C_6H_5 = CH - CH = CH - CH = CH - \underset{\overset{|}{HBr}}{N}HC_6H_5 + H_2NCN$$

Despite the high sensitivity of colorimetric methods of determining pyridine in which cyanogen bromide and aniline are used, these methods have the drawback that they require the use of highly toxic and not so readily available cyanogen compounds. Moreover, in view of the instability, in aqueous solution, of the colored reaction products formed between pyridine, cyanogen bromide, and aniline, it is recommended that the reaction be carried out in a buffer solution [3], or that the colored reaction products be extracted with isoamyl alcohol [2]. It must be subjected to special purification from traces of furfural since furfural gives colored products with aniline under the same conditions.

With the aim of eliminating these drawbacks in the methods of determining pyridine in air, we turned our attention to the reaction which occurs between nicotine, bromothiocyanate reagent, and aniline, described by Shmuk and Borozdina [9].

The chemistry of the reaction of the pyridine nucleus with bromothiocyanate reagent is analogous to the reaction with cyanogen bromide [9,10]; the reaction is characteristic for all bases containing the pyridine nucleus which is, in addition, substituted in the α-position.

Our experiments showed that pyridine gives colored reaction products with bromothiocyanate reagent, which are stable in aqueous media, as well as with bromothiocyanate reagent and alkali without addition of aniline; the sensitivity of these reactions is, however, considerably less than that of the reaction which occurs between pyridine, bromothiocyanate reagent, and aniline. The sensitivity of the latter reaction is 0.005 mg pyridine/5 ml. According to published results, the reaction between pyridine and cyanogen bromide has a similar sensitivity [2]. On the basis of this we came to the conclusion that the reaction between pyridine, bromothiocyanate reagent, and aniline, can be used as a basis for a colorimetric determination of pyridine in air.

All the homologs of pyridine (picoline, lutidine, and collidine) give reactions with both bromothiocyanate reagent plus aniline, and with cyanogen bromide and aniline, but the sensitivity of their reactions is considerably less than in the case of pyridine. Thus, at a concentration of 0.05 mg/ml of a solution of a pyridine homolog, no visually appreciable color is observed, while pyridine itself gives a positive reaction even at a concentration of 0.005 mg pyridine/5 ml. During determinations of 0.005 to 0.05 mg of pyridine, according to our work, pyridine homologs do not give colors with bromothiocyanate reagent and aniline and, consequently, do not affect the accuracy of pyridine determination. Concentration of the vapors of pyridine homologs in the air of industrial establishments, during the use of technical pyridine bases, on account of their lower vapor pressure as compared with that of pyridine, should be several times less than that of pyridine vapor.

The colorimetric method developed can be used for determination of pyridine in the presence of its homologs and quinoline; nicotine interferes. When pyridine bases and nicotine are present at the same time, pyridine and its homologs can be separated from nicotine by well established methods [4,11,12].

Preparation of reagents. 1. A solution of bromothiocyanate reagent is prepared by careful addition (dropwise) of 5% ammonium thiocyanate solution to bromine water, until the bromine water is decolorized. Excess ammonium thiocyanate must be avoided. The solution is kept in the dark in a closed flask.

2. Aniline water is prepared by saturating distilled water with freshly distilled aniline.

3. Standard solution with a concentration of 0.05 mg pyridine/ml is prepared as follows. Into a 100 ml standard flask is introduced a small amount (10-15 ml) of 0.1 N sulfuric acid and the whole weighed; 0.1 ml of pyridine, dried over BaO and redistilled, is added and the whole weighed again. Distilled water is then added to bring the volume up to the mark. From the difference in weight, the pyridine content of 1 ml of the final solution is determined.

The final standard solution is prepared by diluting the solution thus obtained so that 1 ml contains 0.05 mg pyridine.

4. 0.1 N sulfuric acid, neutralized with alkali (to litmus).

Analytical procedure. Air containing pyridine vapor is sucked at the rate of 20-25 liters/hour through two micro-absorbers – Zaitsev type – each containing 2 ml of 0.1 N sulfuric acid. The amount of air drawn through depends on the amount of pyridine it is expected that it contains. The absorbent solutions from the two absorbers are combined in one flask; 2 ml of this combined liquor is taken for analysis. The solution is neutralized with 0.1 N sodium hydroxide (litmus), the volume is noted, and the whole poured into a colorimetric tube. A standard scale is prepared at the same time by adding from 0.1 to 1 ml of the standard pyridine solution (at 0.1 ml intervals) into a series of colorimetric tubes; to all the test tubes of the standard series is then added neutralized 0.1 N H_2SO_4 so as to bring their volumes up to that of test solution; finally, to all the tubes, test as well as standard, is added 0.5 ml of bromothiocyanate reagent and 1 ml of aniline water. The color developed by the test solution is compared with those of the standard series.

Pyridine taken in mg/l	Pyridine found in mg/l
0,0510	0,0510
0,0360	0,0350
0,0348	0,0340
0,0262	0,0250
0,0268	0,0258
0,0268	0,0260
0,0240	0,0230
0,0238	0,0220
0,0134	0,0120
0,0158	0,0160

The accuracy of the method and the completeness of absorption of pyridine from the air were checked as follows: Into a U-tube with fused-off ends but with two outlet tubes, was introduced 1-1.5 ml of pyridine, after which the tube was hermetically sealed and weighed. The weighed tube was connected via one of its outlet tubes and a joint to a Fresenius column containing soda lime and KOH. The other end of the tube was connected to two micro-absorbers – Zaitsev type – each containing 2 ml of 0.1 N sulfuric acid. The absorbers were connected to an aspirator. 1 liter of air was drawn through the system at the rate of 15-20 liters/hour. After the air had been sucked through, the tube was reweighed. The difference in weight gave the amount of pyridine evaporated. The contents of the absorbers were quantitatively transferred to a standard liter flask and water added to bring the volume up to the mark. 1 ml of solution was taken from the standard flask for analysis. Determination of pyridine was then carried out as described above. The results obtained are given in the table.

During development of the method we found that on saturating an aqueous solution of pyridine, or one of its homologs, with hydrogen sulfide, there was formed at first the yellow color characteristic of ammonium polysulfides. Nevertheless, in contrast to ammonium polysulfides, pyridine bases saturated with hydrogen sulfide, after addition of 30-35% sodium hydroxide, formed a green colored solution. This reaction is of low sensitivity, but it may be of some interest for studying the chemical properties of pyridine bases.

SUMMARY

1. A method has been developed for determination of pyridine in air, which is based on reaction of pyridine with bromothiocyanate reagent and aniline.

2. A new color reaction for pyridine bases has been found.

LITERATURE CITED

[1] Lener, Chem. Ztg. 46, 877 (1922).

[2] L. Karlson, J. Appl. Chem. 1, 1, 125 (1931).

[3] R. Fabre, R. Fruhaut and M. Herbert, Ann. pharm. franc. 8, 773, 88 (1950).

[4] L. Barta and Z. Marschek, Biochem. Z. 293, 118-20 (1937).

[5] I. Bouillat, cited in C.A. 45, 9424 (1951).

[6] E. Vongerichten, Ber. 32, 2571 (1899).

[7] S. Saxmoto, cited in C.A. 6542 (1952).

[8] Heterocyclic Compounds (1953), 1, 327-35.

[9] A. Shmuk and A. Borozdina, J. Appl. Chem. 13, 5, 776 (1940).

[10] Yu. Yu. Lurye and V. A. Panova, Factory Lab. 6, 672 (1955).

[11] H. Thoms, Ber. 10, 26 (1900).

[12] A. I. Burshtein, Hygiene of Labor 5, 3-17 (1928).

Received February 21, 1955

BLANK
PAGE

CHRONICLE

ABRAM SEMENOVICH KOMAROVSKY*

(1865–1956)

On May 25, 1956, Professor Abram Semenovich Komarovsky, the oldest analytical chemist in Russia and Doctor of Chemical Sciences, died after a short but serious illness.

Komarovsky was born on December 6, 1865 in Odessa. After finishing at the classical school in Nikolaev, he studied at the natural sciences division in the Physico Mathematical Faculty of Moscow University. In 1888, after participating in "student disorders," which spread to practically all Russian Universities at that time, he was expelled from the University, was excluded from entering any other institutions of advanced teaching, and was placed under police supervision. He received his higher education in Switzerland. After finishing at Zurich Polytechnic, where he worked with Lunge, Treadwell and Hanch, he went to Berne University, where he worked in Kostanetsky's laboratory. In 1893 he defended his thesis on "Benzoresorcinol" for the degree of Doctor of Philosophy.

In his work for this thesis, Komarovsky succeeded in synthesizing this material which hitherto many other research workers had tried to do in vain.

On returning to Russia he came again under police supervision; only in 1897 was he able to go to the newly opened Odessa Central Laboratory of the Ministry of Finance whose director was the liberal professor, A.A. Verigo. From this time to 1922, Komarovsky worked on control in the alcohol and distilling industry. In 1903 he discovered the reaction between aromatic aldehydes and higher alcohols (Komarovsky's reaction), the colorimetric method which he developed on the basis of this reaction for determination of higher alcohols in ethanol was accepted as the official method in many countries. In various modifications Komarovsky's method is still used in analytical practice at present.

In 1910 and 1911 Komarovsky was twice chosen as a private tutor for the Chemical Faculty of Novorossisk University, but his selection was not confirmed by the head of the teaching circle, Komarovsky only managed to get permission to work in P. G. Melikov's laboratory. In this laboratory he worked on peroxide compounds. During his work in this field, he was the first to prepare and describe beryllium peroxide and persilicic acid, and discovered a sensitive reaction for molybdenum with hydrogen peroxide.

He was only able to start teaching after the October revolution, he first became a lecturer at Odessa University, and afterwards a professor in analytical and technical chemistry in the Odessa Advanced Courses for Women and in the Odessa Chemico-Pharmaceutical Institute. A good and demanding teacher, he brought up analytical chemists who have worked successfully in many factory laboratories, higher educational establishments and scientific research institutions.

In 1931, Komarovsky went to work at the Ukrainian Branch of the State Rare Metals Scientific Research Institute, where under his direction, work was carried out on the analytical chemistry of rare elements. p Nitro benzeneazoorcine and chromotrope 2B which were introduced into analytical practice by Komarovsky, are used for the colorimetric determination of beryllium and boron, respectively.

Komarovsky was a member of the International Commission for Checking New Analytical Reactions and Reagents (Nieuwenburg, Bettger, Feigl, Komarovsky, and Strafford) which in 1938 issued its first report (Tables of Reagents for Inorganic Analysis. First Report of the International Committee on New Analytical Reactions and Reagent).

---

*Deceased.

Komarovsky supplied the notes on reactions for rare elements. Further, in Komarovsky's laboratory, experimental verification of reactions published for rare elements during 1910-1935 was carried out. This work, however, was not finished because of the war.

A. S. Komarovsky translated into Russian, and edited more than 10 textbooks, handbooks, and monographs on analytical chemistry. More than one generation of analytical chemists in Russia have been brought up on Komarovsky's translation of "A Course in Analytical Chemistry" by his teacher, Treadwell, to which Komarovsky himself made additions.

A great scientist and a remarkable man, A. S. Komarovsky will be remembered by all who knew him.

CONFERENCE ON THE APPLICATION OF PHYSICOCHEMICAL METHODS OF ANALYSIS AND ORGANIC REAGENTS FOR CONTROL IN THE METALLURGICAL AND METAL WORKING INDUSTRIES

From the 6th to the 8th of June at Dnepropetrovsk a conference was held on the application of physicochemical methods of analysis and organic reagents, for control in the metallurgical and metal-working industries. The conference was called by the Ministry of Crude Metals, Uk. SSSR and the Anal. Chem. Section of the Mendeleev Chemical Society. 335 representatives from 108 factories, 37 towns, various teaching and scientific institutions, were present. 27 reports were read. Some of the reports were of a general and review nature – the problems of analytical chemistry in the light of resolutions passed by the XX Session of the Russian Communist Party; a review of new methods of chemical control in the metallurgical industry; a comparative study of methods of determining arsenic in ores, concentrates, and agglomerates; colorimetric methods of determining barium, strontium, calcium, and magnesium; use of extraction in chemical control of materials of metallurgical production.

Communications on experimental work carried out related to various questions of chemical analysis and control of metallurgical production. A particularly large amount of work had been carried out on the use of photo colorimetric methods of analysis, which had been used before the war on a wide scale in factories and enterprises in Dnepropetrovsk, Zaporozhe, Kirvoi Rog, etc. Noteworthy was the interest displayed by a number of factories in the use of photocolorimetric methods for determining components which occur in large amounts in test materials. The possibility was demonstrated in three reports of carrying out rapid photocolorimetric determinations of silicic acid, aluminum oxides, and iron in slags.

Three reports on methods of determining arsenic in various materials were discussed, as well as three reports on the colorimetric determination of magnesium.

Trilonometric methods of determining calcium, magnesium, iron, other elements have been widely used in factories, as well as extraction methods. These questions evoked great interest on the part of those present. With regard to trilonometric methods, discussion showed that the methods are being successfully used for analyzing various materials. On the other hand, it has been shown, on checking some methods, that they are not reliable. This is explained sometimes by the fact that sufficient emphasis has not been laid on what appear to be small but very important factors. E.g. it is not usually pointed out that the presence of carbonates in the caustic alkali leads to incorrect results for determination of calcium in the presence of magnesium, etc.

Serious attention was also given to the use of physical methods of analysis, e.g. to analysis by reflection of β-radiation, and to questions of automatic control methods. Methods for amperometric titration, electrolytic methods of determining the thickness of galvanic deposits, and other questions were discussed.

It has been decided to issue the scientific reports of this conference as a separate collection. The conference also considered and discussed the work of the journal, "Factory Laboratories." It was suggested that is was desirable to ask the Institute of Scientific Information of the USSR Academy of Sciences to publish a separate book on the divisions of analytical chemistry; the absence of such a publication seriously hinders the wide and rapid use of new results of Soviet and foreign analytical chemistry.

During a discussion on general questions of organization of production control, it was pointed out that in order to speed up smelting it is essential that more rapid methods of analysis be developed, the laboratory quite often holds back production of metal on time. It was also pointed out that the amount of work on physical methods of analysis is small; individual forms of raw materials and products may be rapidly evaluated by using simple physical properties of materials for analysis.

It was also pointed out that a large number of methods have been suggested for some elements, while at the same time little work has been done on a strictly scientific comparison of these various methods. As a result, recommendations for carrying out a particular analysis are of a random character; it is impossible to choose a method which is the most rational under certain conditions. There is no setup in the USSR which can check on the accuracy of these suggested methods, or check proposed changes to State Standards, etc. . A laboratory of standard samples should, above all, study the accuracy of methods for analysis of technical materials. Nevertheless, this laboratory (Sverdlovsk) has not sufficient staff to embark upon important methodological studies. Studies of the comparative value of various analytical methods for a particular element are not undertaken by teaching and scientific institutions either. The conference decided to place before the Commission on Analytical Chemistry of the Academy of Sciences of the USSR questions relating to the organization in the USSR of an establishment which would occupy itself with standardization and unification of analytical methods for raw materials, and for the products of the metallurgical industries.

The conference also noted insufficient provision of laboratory reagents, apparatus and supplies. It was pointed out that in some respects State Standards on apparatus contradict State Standards on analytical methods. Thus, combustion of certain types of steels according to State Standards requires a temperature of 1300-1400°; State Standards on the other hand state that the muffle furnace used should operate at 1200-1250°. On account of poor planning, new forms of apparatus are not issued (e.g. new types of weights); many extremely necessary and readily available reagents such as mandelic acid (for separating zirconium and titanium) are not issued; ion-exchange resins are practically unavailable to laboratories; the supplies of photographic material for spectrographic analysis are inadequate.

ERRATA

No. 3

Russian page	Line	Translation page	Line	What was printed	What should have been printed
342	13	351	37	equal	different

No. 4

Russian page	Line	Translation page	Line	What was printed	What should have been printed
377	7	392	4	2-3 mg	2-3 g

NEW REAGENT

A new, highly sensitive organic reagent for colorimetric determination of gallium –"Gallion IREA" – has been synthesized by the All-Union Scientific Research Institute of Chemical Reagents (IREA).

Organizations and enterprises wishing to test the new reagent can get a free sample if it, together with instructions for its use, by sending a request to the address, "Soyuzreaktivsbyt" (Moscow, Center, Krivokolenny Street, District 12).

In order to decide whether it is worth producing this reagent, it is requested that all who try it out should send, in the course of two months from the date they receive it, detailed accounts of what they think of its practical value, to the address of the Institute of Chemical Reagents (Moscow, Zh-33, Samokatnaya Street, District 4a). The Institute will give advice on any questions relating to the use of Gallion IREA.

At the same time estimates of how much of this reagent is required for the year should be sent to the first address given above so that its production can be organized.

Soyuzreaktivsbyt

ANNOUNCEMENT

The first All-Union Conference on the use of organic reagents in analytical chemistry, called by the Commission on Analytical Chemistry of the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry of the Academy of Sciences of the USSR will take place between the 27th and 30th of November, 1956.

The conference will start on the 27th of November at 17 hours in the Aktov Hall of Moscow State University on the Lenin Heights.

Intending participants should make their reservations by applying to the Institute of Geochemistry and Analytical Chemistry at the following address: Moscow, Vorobyev Road, 47-a, Tel. B-2-05-08 ext. 1-23 and 58.

Organizing Committee

BLANK
PAGE

STUDIES IN THE APPLICATION OF THE COUNTER-CURRENT DISTRIBUTION METHOD

PART 1. A SIMPLE RATIONAL DESIGN FOR THE ELEMENTARY CELL OF A COUNTER-CURRENT DISTRIBUTION APPARATUS

A. S. Khokhlov and V. M. Vaikina

The All-Union Scientific Research Institute on Antibiotics, Moscow

One of the fundamental problems which the chemist encounters, both during the study of natural products, and in the course of synthetic work, is preparation of materials in a pure state and determination of the purity of such materials. In some cases this is very difficult and the use of normal methods of purification (distillation, recrystallization, etc.), and the use of the usual methods of establishing the purity of a material (elemental analysis, determination of melting points and other constants) are not enough. Particularly complex is separation of mixtures of compounds which are of similar structure, and have, as a consequence of this, very similar properties. For separating such mixtures the most widely used methods are the different variants of the chromatographic technique; sometimes electrophoresis can be used with success. Nevertheless, even when such methods are combined, success is not always guaranteed. Accordingly, the method of counter-current distribution [1-5] which is a new method of separating materials which resemble each other closely, is of considerable interest. In some cases, successes have been achieved by this method for separating mixtures, where other methods have failed. This method is gaining in importance, and, thanks to the fact that it allows work on the separation of components to be carried out accurately, the results can be treated mathematically, which means that it becomes possible to analyze mixtures of closely related materials quantitatively.

The counter-current distribution method has found its widest application in the preparation of natural products (in a pure form), from their mixtures and for study of complex mixtures of such materials, and of metabolism products. To illustrate this, we may point out that successful chemical study of antibiotics-polypeptides has only become possible, since, by means of counter-current distribution, some of them were successfully resolved (Gramicidin [6,7]; Tyrocydine [7,8], Nisine [9,10], Polymyxine B [11] and others) into individual materials; other methods including chromatographic techniques had been unsuccessful in these cases. Counter-current distribution has also played an important part in the preparation in a pure form, and the study of a number of other antibiotics (e.g., the Penicillins [12-14], the Streptomycins [15,16], Erythromycin B [17], Magnamycine B [18] et al.). Great advances have also been made in the separation of other natural products—hormonal preparations [19-25], bile acids [26], higher fatty acids [27], porphyrins [28], and many others. Recently papers have been published on the use of this method for separating and determining inorganic materials, e.g., cobalt and nickel salts [29], compounds of the rare earths [30], etc. The counter-current distribution method is also being successfully used for solving problems of a different character. Thus, by means of this technique it is possible to determine accurately the molecular weight of many polypeptides (e.g., Gramicidin C [31], Tyrocydine A [32], Polypeptine [33], etc.) which cannot be done otherwise. Counter-current distribution has been used for studying tautomeric transformations (e.g., Streptomycin [34]), for determining instability constants of complexes [35], and for other purposes.

Counter-current distribution is based on repeated distribution of a mixture of materials (or an individual compound) between two immiscible liquid phases, after which, usually, the light phase is transferred to the heavy phase in the next cell, in which redistribution of dissolved materials starts all over again. At the same time, into all the tubes which the respective light phases have left, and in which there remain heavy phases containing the material dissolved in them, there pass light phases from previous cells, and again redistribution occurs. In this way a counter current is set up—materials which are dissolved in the heavy phase are redistributed in a new portion of light phase (a pure phase is introduced each time into the "zero" cell), while materials dissolved in the light phase are carried forward for distribution in the heavy phase; each time, the light phase moving first during distribution, comes in contact with fresh heavy phase. Redistribution occurs in all cells simultaneously. Since each individual material has, in a given system of solvents (light and heavy phases) its own characteristic distribution coefficient, separation of materials occurs. And, because the distribution coefficient depends to a very large extent on comparatively small differences in structure of the materials, the possibility arises of effecting separation of compounds which resemble each other closely and whose other properties, normally used for separating such materials, are so close to each other as to be of no use.

Counter-current distribution which is based on the same principles as partition chromatography, has a number of advantages over the latter. Without going into details on the characteristics of the different variants of chromatography, two facts stand out. Firstly, mathematical analysis of chromatographic processes has, hitherto, not shown any direct influence on the practical application of these methods since it cannot be used for their objective control. Secondly, the reproducibility of experiments on chromatography depends to a large extent on strict standardization of packing of chromatographic columns (both during adsorption and particularly during partition and ion-exchange chromatography); achieving this strict standardization is sometimes very difficult (See, e.g.,[36]). The counter-current distribution method is free of these drawbacks. Counter-current distribution processes are subject to accurate mathematical control, so that it is possible to make a quantitative evalution of the ratios of the components, not only of those separated, but also of those in the mixture. This is particularly important in those cases where it is not so much a question of separating the components in a pure form, as of making a quantitative evaluation of the composition of the mixture; in such cases it is possible to cut down the time it takes to do an experiment considerably, and to use apparatus which is not very expensive. Counter-current distribution techniques do not require any packing, variations in which from a set standard may interfere with the reproducibility of the work.

The statement on the high efficiency of partition chromatography as a continuous process, as compared with the step-wise method of counter-current distribution, is not in accord with actual results, since, in a number of cases, partition chromatography is less efficient than the counter-current distribution method. By means of the latter method it has been found possible to demonstrate the heterogeneity of preparations of a number of antibiotics-polypeptides, which appeared to be homogenous when examined chromatographically. This can obviously be explained by the fact that during counter-current distribution, the switch to the next stage of the separation occurs after attaining complete equilibrium distribution of the materials between the two phases, while in the case of partition chromatography true distribution between two phases cannot be established.

A characteristic of the counter-current distribution method is that separation of mixtures by means of this technique proceeds under very mild conditions (room temperature, absence of strong reagents, etc.); this means that mixtures which contain very labile components can be separated.

One of the drawbacks of counter-current distribution is the considerable amount of work involved in it, as a consequence of which it is essential to mechanize and automatize the apparatus (which consists of a large number of cells) as much as possible. It should also be noted that carrying out distribution of many compounds is possible only at very low concentrations, since quite often distribution coefficients change at high concentrations, as a consequence of which distribution does not obey mathematical analysis; this is a very valuable characteristic of the method. In order to separate large amounts of pure components, and at the same time maintain conditions such that they can be subjected to mathematical analysis, it is necessary to increase the volume of the cells, as a consequence of which the amount of solvents used increases.

The possibility of using the method is bound up with rapid, reliable, and very sensitive methods of indicating the test components of a mixture. The complexity of the apparatus, which hinders its widespread application, is a drawback of the method. Many types of apparatus have already been described in the literature for counter-current distribution, but they all have drawbacks either in principle or construction.

The first (metal) apparatus [37], did not receive wide application, primarily because of the necessity of having ideally ground basic parts , and because of the limited number of tubes. Another apparatus details of which have been published [38], of fairly simple construction and based on the use of specially curved plastic which was completely stable to the action of various solvents, including organic solvents, is very unreliable. The most widely used apparatus for counter-current distribution is based on glass constructions [1,2,7,39-44]. All of them are made up of collections of up to 220 elementary cells connected in series, and mounted on a frame, which by some sort of mechanism or other, can be rocked within certain limits. The various gadgets used for rocking the apparatus differ from each other only in constructional details, and are of no significance in principle, except in so far as they make the operator's work easier. On the other hand, the construction of the elementary cell itself is of primary importance, since, on its construction depends the efficiency of the apparatus, and the possibility of separating similar materials. Accordingly it is very important to establish what are the basic requirements of an elementary cell.

The fundamental requirement is that the elementary cell should ensure the maximum possible complete and accurate separation of the phases, and permit only one phase to pass on to the next cell, without taking any of the other phase with it. The more thorough this process the more accurate will be the results of counter-current distribution. In addition, the elementary cell should not be very large, and should be convenient for mounting the apparatus, both during operation, and when washing it; it should ensure easy selection of test samples; possible places of contact between organic solvents and rubber or plastic should be avoided in it.

We studied the published constructions for elementary cells in the light of these requirements. It became clear during this study that all the ones we tried failed in one respect or another; in particular it became clear that none of them separate the phases cleanly enough. Thus, during testing of models of elementary cells described in [1,2,7], we found that they do not satisfy completely the basic requirement – quantitative phase separation and transfer of only one phase. It was found that during operation, there was a systematic decrease in volume of the heavy phase as a result of creeping of some drops of the latter along the inner wall of the mixing tube into the connecting tube, from which, together with the light phase, these drops were transferred into the next tube. This transfer of heavy-phase drops cannot be avoided by lengthening the time for which the phases are allowed to separate. Since, it is not drops of heavy phase suspended in the light phase that are transferred into the succeeding tube, but drops of this phase which are formed on the walls of the apparatus as a result of differences in wetting of the walls by the two phases. The shape of the sealed-in tube connecting the mixing tube with the transmitting tube shows a marked effect on this transfer. The smoother the seal (the wider the funnel formed at the joining place), the stronger the washing out of the upper phase. Even if the seal is not in the form of a funnel then the possibility of transfer is only diminished and not removed.

This serious snag which was common to all the constructions described in the literature, was either played down by the authors, or glossed over. Thus, Craig and coworkers, obviously, without finding active measures for preventing this phenomenon of the transfer of drops of the heavy phase attempt to eliminate the visible consequences of this washing out by systematically adding to the "null" cell in a most complex automatic apparatus of 220 cells, not only light phase, but even a small amount of heavy phase. This additional amount of heavy phase introduced into the "null" cell naturally makes up for the loss, but this is only an external correction of the system, since when this is done, the accepted ratio between phases is destroyed, while after establishment of equilibrium concentrations of materials change somewhat. All this, in turn, leads to a change in the amount of material transferred into the neighboring cell, i.e., it leads to a breakdown of the basic condition necessary for accurate mathematical analysis.

This creeping of drops of heavy phase from the mixing tube into the neighboring elementary cell, is obviously one of the reasons for the low accuracy of the counter-current distribution method in practice, as compared with the accuracy expected for this method on the basis of calculation (e.g., Golumbic points out that this method has an error of the order of 3-5%).

This phenomenon is probably responsible for the absence of work on the exact quantitative analysis of mixtures of similar materials by the method of counter current distribution, although it should be very effective for solving such problems.

For two years we have tested in actual practice a new model of an elementary cell which we constructed for counter-current distribution, which was free from the snags common to other, earlier types of cell. This cell (Fig. 1) consists of two parts: the mixing tube A and the transmitting tube B with the connecting tube C. These two parts are connected to each other via a ground glass sleeve, which sticks 4 mm into the mixing tube (when the cell is assembled). The projecting part of the ground sleeve completely prevents the creep of drops of the heavy phase into the adjacent cell and allows one to achieve an extremely accurate separation of top and bottom phases (Fig. 2C). This permits one to get very accurate results.

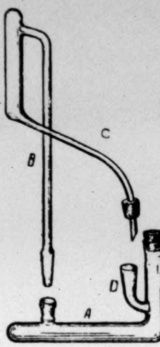


Fig. 1. Elementary cell of a counter-current distribution apparatus A) mixing tube; B) transmitting tube; C) connecting tube; D) sampling tube.

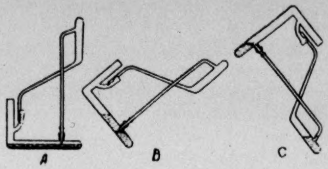


Fig. 2. Movement of the elementary cell during the process of counter-current distribution. A) Position during introduction of test mixture or pure light phase into the "O" cell; B) position during separation of phases; C) position during transfer of the upper phase into the transmitting tube.

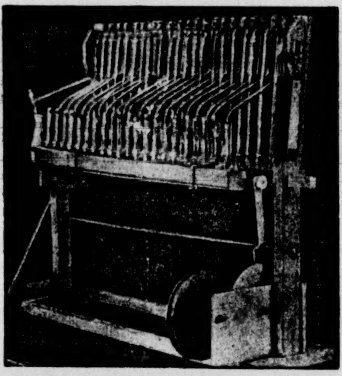


Fig. 3. General appearance of a counter-current distribution apparatus with a flask for taking the upper phase.

The new construction of the dismountable elementary cell has a number of other advantages as compared with other constructions described earlier: it is very easy to mount and wash; it is not fragile; the presence of vertical tubes (Fig. 1,D) permits one to sample any cell readily. The connecting tube C of the transmitting tube is connected to the following mixing tube by a tube E.

Thus, this model of a cell satisfies all the requirements adduced above; at the same time, it is not complicated and can therefore be assembled easily in any glass-working shop having a burnishing lathe.

We worked with an apparatus made up of cells with the following dimensions. The outer diameter of the mixing tube and the transmitting tube was 20 mm. The volume of the lower part of the mixing tube, which determines the amount of heavy phase in the cell, was 10 ml when the tube was at an angle of 140° (Fig. 2,C). The total volume of the mixing tube was 35 ml, whereby it was possible to carry out distribution with a volume of light phase of 3- 20 ml. The height of the vertical tube D (Fig. 1) was 130 mm, the length of the side tube of the mixing tube was 65 mm; its diameter as well as that of the vertical tube was 15 mm with some expansion for the stopper. The volume of the transmitting tube was $\approx$ 30 ml. The tube (Fig. 1) along which the light phase is transferred to the transmitting tube, is fused into the latter at a distance of 3 cm from the top. An elementary cell of the type suggested can be made for dealing with considerably larger volumes of heavy and light phases also without constructional modifications.

Since the first problem that confronted us was determining the purity of materials and determining the composition of mixtures of similar materials without isolating them in an individual state, we used this apparatus with only 21 elementary cells mounted on a wooden frame, rocked by means of an eccentric and rocker (Fig. 3). By means of this apparatus it is possible simultaneously to carry out the intensive mixing of phases in all the cells (which is necessary for redistributing the dissolved phases between the phases), and at the same time, to separate the phases, and finally to transfer only the light phase to the next cell in the series.

The apparatus operates as follows: 10 ml of heavy phase in preliminary equilibrium with light phase (Fig. 2,A) is introduced into all the mixing tubes. Then into the "Null" tube (in Fig. 3, the tube E on the extreme right – without a side tube) the test mixture dissolved in a known volume of light phase is introduced The motor is switched on and the frame rocked (from – 25° (335°) to +50°) for 2 minutes when the motor is switched off and the frame is fixed in the position for the layers to separate (by bringing it up to the first prop) (Fig. 2, B – at a slope of 50°). The phases separate in 5 minutes, after which the frame (together with the elementary cells fixed on it) is let down onto the second prop (Fig. 2, C – at a slope of 140°). When this is done the light phase from all the cells spontaneously flows into the transmitting tube, while the heavy phase remains in the mixing tubes. The apparatus is allowed to rest in this position for 2 minutes so that the light phase may transfer completely into the transmitting tube, while drops of heavy phase creep into the lower part of the mixing tube. As indicated above, these drops cannot get into the transmitting tube since the projecting ground edge stands in their path. The lower part of the projecting edge enables one to separate the slight phase accurately, it then passes into the neighbouring transmitting tube. After completion of the transference of light phase, the frame is returned to its original position (Fig. 2,A); when this is done, the light phase from all the transmitting tubes is transferred into the next mixing tube in the series along tube C (Fig. 1). One cycle of the apparatus has then been completed. Pure light phase is introduced into the "null" cell, and then a second, third, etc., cycle carried out ("transfers").

After 20 cycles ("transfers") the content of each elementary cell can be analyzed, test samples being taken by means of vertical tubes. Nevertheless, in order to increase the resolving capacity of the apparatus, distribution can be carried further; this is done by taking the upper phase from the transmitting tube of the 20 cells after each cycle ("transfer"), using the tap fixed there for that purpose (Fig. 3). This sampling is carried out until all the material introduced into the apparatus has been completely extracted, while the light phase flowing out is completely pure. Completness of extraction is established when the sum total of the amounts of materials in each selected upper phase, as determined by some accepted method of indication (by titration. weighing of the residue, determination of biological activity) is equal to the weight of material introduced into the "null" tube at the beginning of a test. The fact that it is possible to carry out such a check is one of the great advantages of counter-current distribution, since thereby it is possible to control concisely the way in which an experiment is carried out. When the sum total of the weights of material in the individual fractions does not agree with the actual amount of material introduced into the apparatus, this indicates errors, or changes (decomposition) of test material during the experiment; the probability of the latter occurring is very small, since the whole experiment is carried out under very mild conditions.

SUMMARY

An elementary cell of new design is described for counter-current distribution; this cell possesses the following advantages over cells described previously:

1) By introducing a projecting ground edge it has been found possible to prevent gradual creep of drops of heavy phase into the adjacent cell; in other cells this creep has previously led to a gradual decrease in the volume of the lower phase during operation.

2) Owing to this projecting ground edge of the elementary cell, there is a very clear-cut separation of upper phase which ensures high accuracy.

3) The elementary cell has a special vertical tube through which it is possible to take samples without dismantling the whole system. At the same time, these tubes prevent formation of hydraulic shutters.

4) The cell is dismountable so that assembly, operation, and washing are considerably simplified.

LITERATURE CITED

[1] L. C. Craig, Fortschr. chem. Forsch. 1, 292 (1949).

[2] L. C. Craig, and D. Craig., in the book: Technique of Organic Chemistry. (New York and London, 1950) III, pp. 171-311.

[3] E. M. Savitskaya, Antibiotics, VII (XX), 5, 1950.

[4] C. Golumbic, Anal. Chem. 23, 1210 (1951).

[5] H. M. Rauen and W. Stamm, Gegenstromverteilung (1953).

[6] J. D. Gregory and L. C. Craig, J. Biol. Chem. 172, 839(1943).

[7] L. Craig, D. Gregory, and G. Barry, in the book: Amino Acids and Proteins (Moscow, 1952), p. 32.

[8] A. R. Battersby and L. C. Craig, J. Am. Chem. Soc. 74, 4019 (1952).

[9] N. J. Berridge G. G. F. Newton and E. P. Abraham., Biochem. J. 52, 529 (1952).

[10] N. J. Berridge, Nature 169, 707 (1952).

[11] W. Hausmann and L. C. Craig, J. Am. Chem. Soc. 76, 4892 (1954).

[12] C. T. Barry, Y. Sato and L. C. Craig, J. Biol. Chem. 174, 209, 221 (1948).

[13] Chemistry of Penicillin (Princeton, 1949), 1018-1024.

[14] E. P. Abraham, G. G. F. Newton and C. W. Hale, Biochem. J. 58, 94 (1954).

[15] C. W. E. Plaut and R. B. McCormack, J. Am. Chem. Soc. 71, 2264 (1949).

[16] A. E. O'Keefe , M. A. Dolliver and E. T. Stiller, J. Am. Chem. Soc. 71, 2452 (1949).

[17] C. W. Pettinga, W. M. Stark and F. R. van Abeele, J. Am. Chem. Soc. 76, 569 (1954).

[18] F. A. Hochstein and K. Murai, J. Am. Chem. Soc. 76, 5080 (1954).

[19] G. P. Hess, F. H. Carpenter and C. H. Li., J. Am. Chem. Soc. 74, 4956 (1952).

[20] J. G. Pierce, S. Gordon and V. du Vigneand, J. Biol. Chem. 199, 929 (1952).

[21] J. G. Pierce, Biochem. J. 57, 16 (1954).

[22] E. A. Popenoe, H. C. Lawler and V. du Vigneand, J. Am. Chem. Soc. 74, 3717 (1952).

[23] W. F. White, J. Am. Chem. Soc. 75, 503 (1953).

[24] F. A. Kuehl, Jr., M. A. P. Meisinger, N. G. Brink and K. Folkers, J. Am. Chem. Soc. 75, 1953 (1955).

[25] C. J. Migeon, J. Clin. Endocrinol. and Metabolism 13, 674 (1953).

[26] E. H. Ahrens, Jr., and L. C. Craig, J. Biol. Chem. 195, 763 (1952).

[27] E. H. Ahrens, Jr., L. C. Craig, J. Biol. Chem. 195, 299 (1952).

[28] S. Granicks and L. Bogorad, J. Biol. Chem. 202, 781 (1953).

[29] R. Rigamonti, and E. Spaccawella Marchetti, Chimica et industria 36, 91 (1954).

[30] D. F. Peppard, J. P. Faris, P. R. Gray and G. W. Mason, J. Phys. Chem. 57, 294 (1953).

[31] A. R. Battersby and L. C. Craig, J. Am. Chem. Soc. 73, 1887 (1951).

[32] A. R. Battersby and L. C. Craig, J. Am. Chem. Soc. 74, 4023 (1952).

[33] W. Hausman and L. C. Craig, J. Biol. Chem. 198, 405 (1952).

[34] E. Titus and J. Fried, J. Biol. Chem. 174, 57 (1948).

[35] Golumbic and S. Weller, J. Am. Chem. Soc. 74, 3739 (1952).

[36] A. Martin, in the book: Chromatography, Collection 1, (1949), pp. 134-157.

[37] L. C. Craig, J. Biol. Chem. 155, 519 (1944).

[38] G. H. Leids and K. P. Roodswan, Biochem. J. 42, 540 (1951).

[39] L. C. Craig, W. Hausmann, E. H. Ahrens and E. Harfenist, Anal. Chem. 23, 1 236 (1951).

[40] N. Grubhofer, Chem. Ing. Technik 22, 209 (1950).

[41] F. Weygand, Chem. Ing. Technik 22, 213 (1950).

[42] R. Tschesche and H. B. König, Chem. Ing. Technik 22, 214 (1950).

[43] F. A. Metzsch, Chem. Ing. Technik 25, 66 (1953).

[44] M. Verzele, Bull. soc chim Belg. 62, 619 (1953).

[45] A. Kepes, Bull. soc. chim. biol. 35, 10, 1243-1253 (1953).

Received May 31, 1955

BLANK
PAGE

THE USE OF PHYTIC ACID IN THE ANALYTICAL CHEMISTRY OF THORIUM

A. I. Ryabchikov, V. K. Belyaeva and A. N. Ermakov

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow

Phytin has only recently found application in analytical practice, and is better known as a medicinal compound which contains phosphorus.

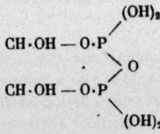
Wheat and rice bran, cotton seed cake and other plant materials serve as raw material for preparing phytin. Phytin is insoluble in water, but dissolves in it readily on addition of mineral acid. On the other hand, phytic acid very readily dissolves in water, alcohol, mixtures of ether and alcohol, and glycerol, but does not dissolve in benzene, chloroform, or glacial acetic acid. Phytic acid has not been prepared in a crystalline form.

A large number of articles have been devoted to the study of the composition of phytin; nevertheless, data on its structure is very contradictory. Apparently, phytin is a mixture of the calcium-magnesium salts of inositol-pyrophosphoric acid.

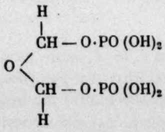
In 1872, Pfeffer [1] described some characteristic inclusions of aleuronic grains – globoids – and established that they consisted of the calcium-magnesium salts of phosphoric acid combined with an organic substance. Later, Palladin indicated [2], that this substance is contained in appreciable amounts in the globoids of the aleuronic grains of almost all cereals.

First studies of globoids were carried out by Schulze and Winterstein [3-5], and also by Posternak [6-10]. It was found that the material contained in the seeds of these plants contained up to 90% of the total phosphorus. The material was given the name phytin. On the basis of elemental analysis, the empirical formula $C_2H_8P_2O_9$ was ascribed to phytin.

After studying the chemical properties of phytin (behavior towards alkalis, and mineral acids; break down to give inositol and phosphoric acid on heating), Posternak [8,9], proposed the following structural formulas:



and



The author assumed that inositol is not an actual component of phytin, but is formed as a result of the interaction of the latter with water on heating:

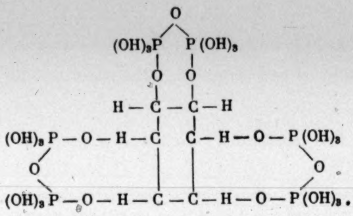
$$3C_2H_8P_2O_9 + 3H_2O = 6H_3PO_4 + 6CH_2O$$

$$\underline{6CH_2O = C_6H_{12}O_6}$$

$$3C_2H_8P_2O_9 + 3H_2O = (CHOH)_6 + 6H_3PO_4$$

Other authors [11-13], got results which seemed to agree with Posternak's theory. Nevertheless, further work led to a convincing overthrow of this conception of the structure of phytin. It was shown [14-17], that inositol is actually a component part of phytin. Proof of this was the discovery by Neuberg [15] of the formation of furfural during direct distillation of phytin. He obtained similar results on distilling inositol with phosphorus pentoxide [17].

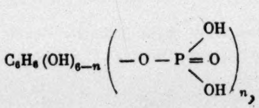
The incorrectness of Posternak's hypothesis was even more clearly demonstrated by the enzymatic cleavage of phytin to yield inositol [16]. In the given instance, phytin was regarded as the ester of inositol with hexaphosphoric acid. On the basis of these facts, Neuberg suggested that Posternak's formula should be trebled – $C_6H_{24}O_{27}P_6$ – and ascribed the following structural formula to phytin:



The presence of inositol in phytin has not been disputed since. A number of research workers have prepared phytin synthetically from inositol and orthophosphoric acid[18-21]. Nevertheless, there is still no unanimous agreement about the composition of phytin.

Thus, Anderson [22], stated that phytin isolated from wheat grains contained pentose. In later papers the presence of a number of inositolphosphoric acids in cereals has been indicated [23]; these include: inositolmonophosphoric, inositoltriphosphoric [24-25], inositolhexaphosphoric [26], and also inositolpentaphosphoric acids [27,28]. Meanwhile, the presence of penta, tetra, and other lower acids has been explained by partial hydrolysis of inositolhexaphosphoric acid [29]. This diversity has also been explained by the possible influence of the type and quality of the original raw material, and the method of extraction, on phytin composition [30].

Thus, for a long time it has been reckoned that phytin available commercially is a mixture of the Ca - Mg salts of inositolphosphoric acids of the following composition:

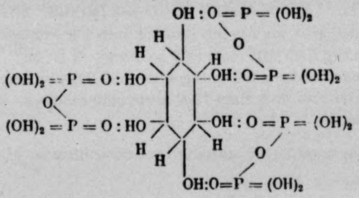


$$C_6H_6(OH)_{6-n}\left(-O-P\overset{OH}{\underset{OH}{=}}O\right)_n,$$

where n can have values from 1 to 6, while inositolhexaphosphoric and inositolpentaphosphoric acids respectively, predominate [31-33]; the possibility that pyrophosphoric acid is also a component of phytin is not excluded either [29,30,34]. Starkenstein [35], who studied the behavior of phytin during titration with uranyl acetate and silver nitrate, pointed out the existence of pyrophosphoric acid in phytin. According to his results, the formula of phytin should be represented as inositolpyrophosphoric acid.

The problem of the type of phosphoric acid in phytin can be solved by comparing the behavior of phytin with the salts of various phosphoric acids. Of interest in this connection is the work of Beck [36-38], who used the sodium salt of phytic acid for quantitative determination of scandium in plant and animal organisms. It was found that scandium phytinate has much in common with scandium pyrophosphate. They are both insoluble in mineral acids, while scandium orthophosphate readily dissolves even in dilute acids.

On the basis of comparisons of the properties of the pyrophosphates and phytinates of a number of metals, Beck reckons that phytic acid is an ester of inositol and pyrophosphoric acid:


OH : O = P = (OH)₂
H
O
H
H
(OH)₂ = P = O : HO
OH : O=P = (OH)₂
O
(OH)₂ = P = O : HO
OH : O = P = (OH)₂
H
H
O
H
OH:O=P = (OH)₂

The correctness of the hypothesis on the presence of pyrophosphoric acid in the phytin molecule is further confirmed by the fact that 12 basic salts are known. This signifies that all the four hydrogen atoms in each of the three pyrophosphoric acid groups can be substituted by a metal; if on the other hand phytin were an inositolhexaphosphate one would expect 18 basic salts.

Thus, apparently, the hypothesis that pyrophosphoric acid is linked to inositol via two hydrogen bridges is correct. This property of pyrophosphoric acid to form hydrogen bridges has been demonstrated previously by Schwarzenbach [39].

Phytin has been used for analytical purposes by I. P. Alimarin and L. Z. Kozel for quantitative determination of zirconium [40], and other elements, in a number of objects.

Qualitative Reactions with Phytic Acid

A study has been made of the interaction of phytic acid with most inorganic cations, with the exception of platinum group elements.

Phytic acid was made from commercial phytin by means of ion exchange. Cation exchange resin KU-2 in the hydrogen form was used.

50 g of powdered phytin was dissolved in 400 ml water containing 22 ml of concentrated hydrochloric or nitric acid, after which the solution was filtered to remove insoluble residue. Under these conditions the pH of the solution varied from 4.8-5.0. The phytin solution was passed through a layer of ion-exchange resin at the rate of 0.5 ml/minute/cm^2 (column length–1000 mm, diameter 30 mm, volume of KU-2 resin–200 cm^3). The column was washed with distilled water. The total volume of acid obtained in this way was 600-800 ml with a concentration of 40-50 mg/ml. A qualitative criterion of the removal of calcium and magnesium ions was the absence of a precipitate on neutralization of phytic acid with ammonia.

In experiments on precipitation of various elements by phytic acid, 10 ml of a solution of the respective salt containing 1 mg/ml (calculated on the basis of the metal) was taken.

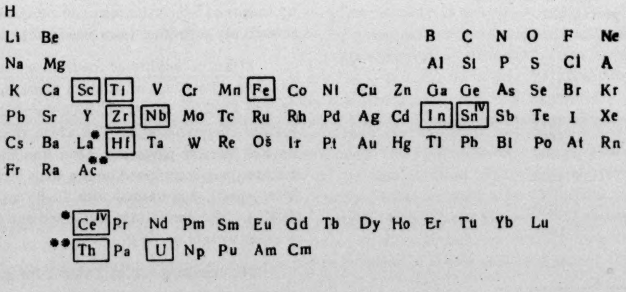

H
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Pb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn^IV Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac**
*Ce^IV Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tu Yb Lu
**Th Pa U Np Pu Am Cm

Fig. 1. Precipitation of elements by phytic acid from 1 N nitric acid.

From neutral solutions, phytic acid precipitates almost all the elements except the alkali metals. The picture changes sharply on acidifying the solution with mineral acid. Thus, from 1 N nitric acid solutions, Ti, Zr, Hf, Th, Ce^{IV}, Nb, U, Sc, In, Sn^{IV} and Fe (see Fig. 1) are precipitated. It is interesting to observe that In and Sn^{IV}, at the concentrations indicated, are not precipitated from 1 N hydrochloric acid. Selectivity is more clearly demonstrated on precipitating from still more acid solutions. E. g., Sn^{IV} and Fe do not give a precipitate with phytic acid, if the concentration of the solution is greater than 2N with respect to nitric acid, while Ti, Zr, Hf, Th, Ce^{IV}, In, and Sc are precipitated even from 12 N nitric acid solutions. Accordingly, this reagent shows great selectivity in strong solutions.

We studied the conditions for quantitative separation and determination of thorium in more detail.

Determination of Thorium in Monazites*

During determination of thorium in Monazites (4-12% Th) the most arduous and difficult work is its separation from the rare earths.

The methods used at present for this purpose are based on precipitation of thorium from strong acid solutions. Under these conditions, differences in the solubility of the corresponding compounds of thorium and the rare earths are more sharply expressed, adsorption of other ions is practically absent, and analysis can be carried out more rapidly, owing to the smaller number of operations.

The most widely used method for the quantitative determination of thorium is the classical iodate method of Meyer and Speter [41], based on precipitation of thorium as the iodate from a solution of nitric acid 40% (by volume). This method has been modified by Yu. A. Chernikhov and T. A. Uspensky [42], who developed a variant for the volumetric determination of thorium, by titrating iodate combined with thorium with sodium thiosulfate.

Precipitation of thorium with potassium iodate was used for determining small amounts of thorium in natural materials [43].

It should be noted however that other 4-valent elements – Zr, Ti, Ce^{IV}, and U^{IV}, purification from which is realized with oxalic acid, are precipitated with thorium by iodate. In this connection, of interest is work in which the authors recommend precipitation of thorium by potassium iodate from 40% (by volume) HNO_3 in the presence of oxalic acid [44]. When this is done, Zr, Ti, and Bi remain in solution in the form of stable oxalate complexes.

From strongly acid media, thorium can be isolated with pyrophosphate [45-47], hypophosphate [48-50], metaphosphate, and double phosphate [51], and also by sodium fluorosilicate [52]. Of these, the most widely used is the pyrophosphate method which is based on separation of thorium from 0.3 N HCl. This method however has no advantages over the iodate method. Losses of thorium as the result of formation of a soluble complex $Na_4[Th(P_2O_7)_2]$ in the presence of excess precipitant are possible.

TABLE 1
Precipitation of Th from Nitric Acid Solutions
(0.0701 g Th)

HNO_3 concentration, N	Weight of calcined precipitate, in g
2	0.1626 0.1634 0.1634
4	0.1617 0.1647 0.1633
6	0.1633 0.1630 0.1630
8	0.1631 0.1636 0.1635
Mean	0.1632

More detailed procedures of numerous methods for determining thorium in various materials have been brought together in a series of monographs [52-54].

Phytic acid also belongs to that number of reagents by means of which thorium can be quantitatively and selectively separated from strong acid solutions.

Effect of acidity of medium on separation of thorium. To 70 ml of solution containing ~ 1 mg/ml Th and a known excess of HNO_3 (or HCl), was added 5 ml of 4% phytic acid. The white amorphous precipitate of thorium phytinate, after standing for 15-20 minutes, was transferred onto a blue ribbon (a grade of filter paper), and washed with 70-80 ml of 1 N HCl (HNO_3). The precipitate was dried and then calcined to constant weight at 1100°.

The results given in Table 1 for gravimetric determination of thorium show that over a wide acidity range no appreciable amount of thorium phytinate dissolved.

---

* V. I. Naumova took part in the experimental side of the work.

Effect of excess phytic acid. To 70 ml of a 2N HNO_3 solution containing ~ 1 mg/ml of Th, was added a known amount of phytic acid. After 15-20 minutes, the thorium phytinate precipitate was filtered and washed with 70-80 ml of 1 N HNO_3 solution. Experimental results are given in Fig. 2. These results show that the precipitate of thorium phytinate hardly dissolves at all even in a 6-fold excess of phytic acid. An eight fold excess of precipitant causes only a slight amount of the precipitate to dissolve (~ 2%).

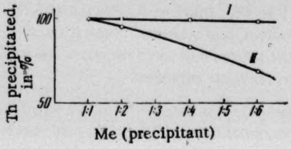


Fig. 2. Effect of excess precipitant (in comparison with the stoichiometric amount) during precipitation of thorium with phytic acid (I) and sodium pyrophosphate (II).

It is interesting to compare these results with results obtained during precipitation of thorium with sodium pyrophosphate (See Fig. 2). Even a 2-fold excess of pyrophosphate leads to incomplete separation of thorium, while when a 6-fold excess is used, only 70% of metal is precipitated. Precipitation of thorium by pyrophosphate was carried out from 0.3 N HCl, as recommended in the literature [44].

Apparently, the bond between the pyrophosphate ion and inositol in the molecule of phytic acid suppresses its complexing properties considerably, thereby facilitating choice of optimum conditions for quantitative separation of thorium.

Composition of the residue after calcining thorium phytinate. The experiments described above on precipitation of thorium by phytic acid showed good agreement between the gravimetric determinations, thereby testifying to the constancy of the composition of the residue.

From the results given in Table 2 it follows that the residue from calcining thorium phytinate contains 42.9% of Th (i.e. the factor for converting to metal is 0.429), which corresponds best of all to the formula $ThO_2 \cdot 2P_2O_5$ (See Table 3).

TABLE 2

Th Content of the Calcined Residue

Weight of calcined residue, in g	Th content of residue in %
0.1548	42.96
0.1549	42.93
0.1550	42.90
0.1541	43.15
0.1556	42.73
0.1544	43.06
0.1547	42.98
0.1553	42.82
0.1558	42.68
Mean 0.1549	42.91

TABLE 3

Calculated Th Content in Various Compounds

Proposed formula of the calcined residue	Calculated Th content, in %	Deviation from experimental results, % absolute
$2ThO_2 \cdot 3P_2O_5$	48.6	−5.7
$ThO_2 \cdot P_2O_5$	57.1	−14.2
$ThO_2 \cdot 2P_2O_5$	42.3	+ 0.6

The calcined residue is not hygroscopic and consequently does not contain free P_2O_5. Presumably the calcined residue is thorium metaphosphate.

The possibility that the residue formed in the given instance is thorium metaphosphate is confirmed by numerous published results on its production during high temperature processes. Thus, Trost and Ouvrard [55] obtained thorium metaphosphate by the action of dry $ThCl_4$ or $ThBr_4$ on molten metaphosphoric acid. Johnson [56], prepared $Th(PO_3)_4$ by a reaction between phosphoric acid and thorium sulfate at a red heat.

The experimental results adduced above enable us to conclude that 3 ions of thorium are connected to two phytic acid residues. The correctness of this assumption is confirmed by experiments on the quantitative determination of thorium directly as thorium phytinate. For this purpose, thorium phytinate precipitated from 2N nitric acid solution was filtered through a No. 3 sintered glass crucible filter weighed beforehand, and dried at 105-110° to constant weight in a drying oven. The results of three parallel tests (Table 4) correspond best to the theoretical ratio of thorium to phytic acid of 3:2. In the given instance, phytic acid behaves like a 6-base acid, in accordance with the conclusions of Starkenstein [35] which he based on titration of phytic acid with uranyl acetate.

TABLE 4

Composition of Thorium Phytinate (0.0653 g taken)

Th Phytinate obtained in g	Theoretical Amount of phytinate for Th:Phytinate ratios of		
	3:1	2:1	3:2
0.2066			
0.2050	0.1311	0.1646	0.1981
0.2070			

TABLE 5

Determination of Th in the Presence of Al, Fe, Ca, La, Ce, Nd, U, Ti

Th taken in g	Me taken in g	Ratio of Th:Me	Weight of precipitate	Th found in g	Relative error, %
	Al				
0.0646	0.12	1:2	0.1500	0.0644	0.3
0.0646	0.50	1:8	0.1483	0.0628	3.0
	Fe				
0.0646	0.0093	7:1	0.1698	0.0729	13.0
	Ca				
0.0646	0.011	6:1	0.1499	0.0643	0.5
	La				
0.0646	0.4488	1:7	0.1499	0.0643	0.5
	Ce				
0.0646	0.0599	1:1	0.1492	0.0640	1.0
0.0646	0.2995	1:4.6	0.1501	0.0644	0.3
	Nd				
0.0646	0.20	1:3	0.1510	0.0648	0.3
	U•				
0.0646	0.0785	1:1.2	0.1518	0.0651	1.4
0.0646	0.1570	1:2.4	0.1537	0.0659	2.0
	Ti••				
0.0646	0.0133	5:1	0.1546	0.0663	2.6
	0.0033	20:1	0.1521	0.0652	1.0

• Precipitation from 6N HCl.

•• Precipitation in presence of H_2O_2.

Determination of thorium in the presence of the rare earths, Al, Ca, Fe, U, Ti, Zr. According to semi-quantitative spectrographic analysis, monazites contain appreciable amounts of rare earths (~ 60%), thorium (1-7%), silicon (~ 2%), phosphorus (~ 10%), aluminum (~ 2%), calcium (~ 2%), magnesium (~ 2%), iron (~ 0.5%), and also titanium, zirconium, and uranium. Separation of thorium in the presence of these elements was studied first of all on synthetic mixtures.

Thorium was precipitated from 100 ml of 6 N HNO_3 by addition of 5 ml of 4% phytic acid, according to the method described; the ratio of Th:Me exceeded the ratios in natural materials. Results are given in Table 5.

The most difficult part of the operation—separation of thorium from rare earths— was solved fairly easily in the present case: after one precipitation, practically complete separation was effected. Spectrographic examination of the residue after calcining the thorium phytinate precipitate showed that the content of rare earths at ratios of Th:Me > 1:3, amounted to 0.1 - 0.3 %. At lower ratios of Th:Me, the precipitate contained less than 0.1% of rare earths as impurity. Aluminum and calcium do not interfere with the quantitative determination of thorium. Iron is coprecipitated to an appreciable extent with thorium, rather surprisingly, since phytic acid does not precipitate such small amounts of iron (0.1 mg/ml) from pure solutions, even from 2 N HNO_3. Uranium, titanium, and zirconium are completely precipitated during precipitation of thorium from nitric acid solutions. Coprecipitation of titanium can be avoided by precipitating thorium in the presence of H_2O_2 which simultaneously serves as a reducing agent for quadrivalent cerium. Uranium can also be separated from thorium by precipitating the latter from 6 N HCl. Nevertheless, the best method of separating thorium from zirconium, titanium, uranium, and iron proved to be that using oxalic acid. Preliminary tests showed that precipitates of the phytinates of Zr, Ti, U, and Fe dissolve readily in oxalic acid, forming stable oxalate complexes, which are stable even in strongly acid media. Table 6 contains results for quantitative determination of thorium in the presence of oxalic acid. In each test, precipitation of thorium was carried out from 100 ml of 6 N HNO_3, containing 25 ml of 10% oxalic acid. In this case completely satisfactory separation of thorium was achieved.

Similar results were obtained during precipitation of thorium by phytic acid followed by treatment of the precipitate with oxalic acid.

During determination of thorium in monazite concentrates it is expedient to carry out a supplementary purification from impurities by reprecipitation of thorium phytinate. The precipitate was dissolved in a saturated solution of disubstituted ammonium citrate, and the necessary amounts of concentrated nitric acid and 4% phytic

TABLE 6

Separation of Th from Fe, Ti, Zr, and U in the Presence of $H_2C_2O_4$

Th taken in g	Me taken in g	Ratio Th : Me	Wt. of precipitate in g	Th found in g	Relative error in %
0.0653	—	—	0.1523	0.0653	0.0
0.0653	—	—	0.1534	0.0658	0.8
0.0653	—	—	0.1526	0.0655	0.3
	Zr				
0.0653	0.010	6.5 : 1	0.1546	0.0663	1.5
0.0653	0.010	6.5 : 1	0.1534	0.0658	0.8
0.0653	0.010	6.5 : 1	0.1538	0.0660	1.2
0.0653					
	U				
0.0653	0.010	6.5 : 1	0.1525	0.0654	0.2
0.0653	0.010	6.5 : 1	0.1536	0.0659	1.0
0.0653	0.010	6.5 : 1	0.1523	0.0653	0.0
	Fe				
0.0653	0.010	6.5 : 1	0.1539	0.0660	1.1
0.0653	0.010	6.5 : 1	0.1527	0.0655	0.3
0.0653	0.010	6.5 : 1	0.1515	0.0650	0.5
	Ti				
0.0623	0.010	6.2 : 1	0.1467	0.0629	1.0
0.0623	0.010	6.2 : 1	0.1433	0.0615	1.3

TABLE 7

Reprecipitation of Thorium Phytinate in the Presence of Disubstituted Ammonium Citrate (0.0646 g Th taken in each case)

Volume sat. soln. $(NH_4)_2$Cit, in ml	Wt. calcined residue	Th found in g	Relative error in %
20	0.1498	0.0643	0.5
20	0.1503	0.0645	0.2
40	0.1495	0.0641	0.8
60	0.1502	0.0644	0.3
80	0.1511	0.0648	0.3
100	0.1497	0.0642	0.6
100	0.1510	0.0648	0.3
100	0.1509	0.0647	0.2

TABLE 8

Determination of Th in Monazite Concentrates

Sample No.	Determined by phytic acid method				Th found by iodate method in %
	Weight of residue in g	Th content of residue in g	Th content of concentrate, %		
1	0.1613	0.0692	6.9	7.0	6.9
	0,1635	0.0701	7.0		
	0,1622	0.0696	7.0		
2	0.1255	0.0538	5.4	5.5	5.5
	0.1294	0.0555	5.6		
	0.1290	0.0553	5.5		
3	0.1157	0.0496	5.0	5.1	5.0
	0.1182	0.0507	5.1		
	0.1184	0.0508	5.1		
4	0.1415	0.0607	6.1	6.1	6.0
	0.1443	0.0619	6.2		
	0.1426	0.0612	6.1		

acid were added respectively. When this is done, thorium is reprecipitated as the phytinate. Completeness of thorium precipitation in the presence of $C_6H_6O_7(NH_4)_2$ was checked beforehand on pure solutions. As can be seen from the results given in Table 7, loss of thorium during one reprecipitation is not observed even in the presence of a large excess of ammonium citrate.

A method of determing the thorium content of monazite concentrates. On the basis of studies of the conditions for quantitative separation of thorium from synthetic mixtures, a technique was developed for determination of thorium in monazite concentrates.

The test sample (weight 10g) was broken down with sulfuric acid by the usual method [45]. After a two-fold leaching of the sulfates with ice water, the volume of solution amounted to 500-600 ml, and then made up to 1 liter with concentrated nitric acid.

100 ml of the solution thus obtained was transferred to a 150 ml beaker, and 1-2 ml of 30% hydrogen peroxide added; the solution was heated and 25 ml of 10% oxalic acid added. Thorium was precipitated from this solution

by adding 5 ml of 4% phytic acid. After 15-20 minutes, the precipitate was separated by centrifuging (volume of test tube 50 ml, number of revolutions/minute 3000-3500), washed twice, and centrifuged in a 25 ml test tube with the wash liquor,* and dissolved in 15-20 ml of a saturated solution of disubstituted ammonium citrate. The solution thus obtained was transferred to a 150 ml beaker, the test tube rinsed out with 25-30 ml water, after which, to the combined solution was added 30-40 ml concentrated HNO_3, 1 ml of 30% hydrogen peroxide, and 4-5 ml of 4% Phytic acid. After 15-20 minutes, the precipitate was filtered through a blue ribbon filter, washed 4-5 times with 4 N HNO_3, transferred to a weighed crucible, dried, and finally calcined in a muffle operating at 1100°, to constant weight.

Table 8 contains the results obtained during determination of thorium in a number of monazite concentrates (conversion factor to thorium 0.429).

The results obtained were compared with results obtained for the same samples using the classical iodate method. As is evident from Table 8, the phytic acid method is no less accurate than the iodate method. The phytic acid method however cuts down the time required for an analysis by a half. The accuracy of the method is ± 0.1% absolute, which for a thorium content of 4-7% in Russian samples, corresponds to 2% relative.

Phytic acid, undoubtedly, will find wide application in analytical practice. It has been shown in preliminary experiments that it should be possible to use it for concentrating scandium from mineral raw material using thorium as a carrier. There is a possibility of determining cerium by means of phytic acid in various materials, including monazites (in the filtrate after removing thorium). At the same time, information on the composition and structure of phytin is too contradictory, and it is essential to make a more detailed study of this interesting reagent.

SUMMARY

1. A qualitative study has been made of the interaction of phytic acid with most of the elements in the periodic system, and conditions have been established for quantitative separation of thorium in which phytic acid is used as precipitant.

2. It has been established that the composition of the residue left after calcining thorium phytinate at 1100° corresponds to the formula $Th(PO_3)_4$.

3. It has been demonstrated that it is possible to separate and determine thorium quantitatively by means of phytic acid in the presence of oxalic acid, which is a complexing agent for titanium, zirconium, uranium, and iron.

4. A technique has been worked out for quantitative determination of thorium in monazite concentrates; this is based on precipitation of thorium from 6 N (by volume) nitric acid in the presence of oxalic acid.

LITERATURE CITED

[1] W. Pfeffer, Jahrb. Wiss. Botan. 8, 147 (1872).

[2] V. M. Palladin, Z. Biol. 31, 191 (1894).

[3] E. Schulze and E. Winterstein, Z. physiol. Chem. 22, 90 (1896).

[4] E. Winterstein, Ber. 30, 2299 (1897).

[5] E. Schulze and E. Winterstein, Z. physiol. Chem. 40, 120 (1903).

[6] M. S. Posternak, Revue generale de botanique 12, 5 (1900).

[7] M. S. Posternak, Compt. rend. 137, 202 (1903).

[8] M. S. Posternak, Compt. rend. 137, 337 (1903).

[9] M. S Posternak, Compt. rend. 137, 439 (1903).

[10] M. S. Posternak, Compt. rend. soc. biol. 55, 1190 (1903).

---

* Composition of wash liquor: 25 ml 4% phytic acid, 25 ml 10% oxalic acid, and 300 ml concentrated nitric acid, per liter of solution.

[11] A. J. Patten and E. B. Hart, Am. Chem. J. 31, 564 (1904).

[12] E. B. Hart and W. E. Tottingham, J. Biol. Chem. 6, 431 (1909).

[13] R. J. Anderson, J. Biol. Chem. 11, 471 (1912).

[14] C. Neuberg, Biochem. Z. 5, 443 (1907).

[15] C. Neuberg, Biochem. Z. 9, 560 (1908).

[16] Susuki, Voshimura, Takaishi, Bull. Coll. Agr. Tokyo. Imperial University 7, 503 (1907).

[17] C. Neuberg, Biochem. Z. 9, 551 (1908).

[18] A. Contardi , J. C. C. 1, 1032 (1910).

[19] R. Anderson, J. C. C. 2, 504 (1912).

[20] M. S. Posternak, Compt. rend. 168, 1216 (1919).

[21] M. S. Posternak, Compt. rend. 169, 34, 188, 337 (1919).

[22] R. J. Anderson, N. Y. (Geneva). Expt. Sta. Tech. Bull. 32 (1914).

[23] R. J. Anderson , J. Biol. Chem. 18, 425 (1914).

[24] R. J. Anderson, J. Biol. Chem. 18, 441 (1914).

[25] R. J. Anderson , J. Biol. Chem. 20, 463 (1915).

[26] R. J. Anderson , J. Biol. Chem. 17, 141 (1914).

[27] J. B. Rather , J. Am. Chem. Soc. 39, 777 (1917).

[28] J. B. Rather , J. Am. Chem. Soc. 40, 523 (1918).

[29] R. J. Anderson , J. Biol. Chem. 44, 429 (1920).

[30] K. A. Krasysky, Ukrainian Chem. J., Tech. Section 1, 11 (1925).

[31] E. A. Litkins, Food Ind. 9-10, 297 (1926).

[32] Pharmaceutical Preparations, Notebook (United Sci. Tech. Press, 1934).

[33] T. Jenkins and U. Hartung, Chemistry of Organic Medicinal Preparations (Foreign Lit. Press, Moscow 1949).

[34] R. Anderson, J. C. C. 2, 825 (1912).

[35] E. Starkenstein, Z. Biochem. 30, 56 (1911).

[36] G. Beck, Mikrochem. 34, 62 (1948).

[37] G. Beck, Mikrochem. 34, 282 (1949).

[38] G. Beck, Mikrochem. 36/37, 790 (1951).

[39] G. Schwarzenbach, Monatsch. 81, 202 (1950).

[40] I. P. Alimarin and L. Z. Kozel, Collection: Chemistry of Rare Elements, No. 3 (In the press).

[41] R. J. Meyer and M. Speter, Chem. Z. 34, 398 (1910).

[42] Yu. A. Chernikhov and T. A. Uspenskaya, Factory Lab. 9, 276 (1940).

[43] F. S. Grimaldi, Irving May, M. H. Fretcher and J. Fitcomb , Geological Survey Bulletin, 1006 (United State Government Printing Office, Washington, 1954).

[44] M. M. Tillu and V. T. Athavale, Anal. Chim. Acta 11, 62 (1954).

[45] R. J. Carney and E. D. Campbell, J. Am. Chem. Soc. 36, 1134 (1914).

[46] V. F. Gillebrand and G. E. Lendel, Practical Textbook on Inorganic Analysis (United Sci. Tech. Press, 1937) p. 57.

[47] T. Moeller and D. Schweizer, Anal. Chem. 20, 1201 (1948).

[48] C. Winkler, Ber. 24, 885 (1881).

[49] M. Koss, Chem. Z. 36, 686 (1912).

[50] A. Rosenheim, Chem. Z. 36, 821 (1912).

[51] L. W. Ryan, Chem. Zentr. 2, 1126 (1922).

[52] T. Moeller, D. Schweizer and D. Starr, Chem. Revs. 42, 63 (1948).

[53] C. J. Rodden and J. C. Warf, Analytical Chemistry of the Manhattan Project, Div. VIII, 1, 160 (1950).

[54] W. Fresenius and G. Jander, Handbuch der analytischen Chemie, IVb,303 (1950).

[55] L. Trost and L. Ouvrard, Compt. rend. 105, 30 (1887).

[56] K. R. Johnson, Ber. 22, 976 (1889).

Received June 18, 1956

POTASSIUM TETRABORATE AS A PRIMARY STANDARD IN ACIDIMETRY

Ya. Ya. Sauka and Ya. K. Putnin

Latvian State University, Riga

At present there are quite a few bases which have been suggested for standardizing strong acids, e.g., sodium carbonate, borax, sodium oxalate, etc. [1]. Without going into a detailed consideration of the well known properties of these bases, their advantages and drawbacks, it should be noted that, at present, there is no substance which satisfies all the requirements which primary standards should meet in acidimetry.

The authors do not believe that potassium tetraborate completely answers all requirements, but in comparison with the bases mentioned above, this compound has undoubted advantages.

Atterberg [2], was the first to prepare potassium tetraborate. It separates out from solutions whose composition varies from tetraborate to diborate [2,3]. When there is a large excess of K_2O, diborate may separate out; when the K_2O content is low, the tetraborate. In order to ensure formation of pure potassium tetraborate, a 10-20% excess of K_2O is necessary.

The necessary starting materials for synthesizing potassium tetraborate are boric acid and either potassium carbonate or potassium hydroxide. To a boiling solution of boric acid (100 g H_3BO_3 in 100 ml water; all the boric acid does not dissolve) is added gradually 60-65 g of K_2CO_3. The potassium carbonate should be added slowly, in small portions. If this is not done the solution will become alkaline owing to excess K_2CO_3, evolution of carbon dioxide will cease, and consequently potassium tetraborate will not be formed. To prevent crystals from clustering together, a mechanical stirrer is placed in the solution, and by gentle heating the temperature is raised so that towards the end of the crystallization process, with the object of avoiding formation of hydrates with high water content [3,4], it is not less than 30°. Approximately after 1/2 – 1 hour, the first cyrstals start to crystallize out as beautiful prisms. The crystallization process can be regarded as complete at the end of 3 hours. Tetraborate crystals are filtered off and washed with small amounts of water. The product thus prepared is not quite pure, accordingly it is recrystallized twice from hot solutions (100 g of $K_2B_4O_7 \cdot 4H_2O$ in 100 ml water); during the second crystallization, crystals are washed with alcohol and ether. Preparations which contain water, on drying pick up carbon dioxide from the air and become contaminated with carbonate. Alcohol and ether are removed by drying the crystals at 50-60°.

The purity of the potassium tetraborate was checked by determining water content and K_2O. Water was determined by calcining in a crucible until the compound clinkers; the K_2O, by titration with 0.1 N HCl using Methyl Red as indicator.

	Found %	Calculated %
H_2O	23.59	23.59
K_2O	30.83	30.83

Slightly higher water contents were found for preparations dried at room temperature (23.61 and 23.62%).

Water of crystallization (four molecules) is very firmly held. 5 g of material was heated in a weighing bottle in an air oven, the temperature being raised stepwise every five hours. Results of dehydration are given in Table 1.

As shown in the Table, a preparation loses only 0.07% after heating for 5 hours at 75°. Even at 100°, for the same length of time, the preparation only lost one fifth of its water. On standing in air (relative humidity 70%) this lost water is made up in the course of a few hours. In view of this, potassium tetraborate can be dried to 65° without any danger of losing part of its water of crystallization. Constant weight is attained under these conditions in 3-4 hours.

TABLE 1
Dehydration of Potassium Tetraborate Tetrahydrate (~ 5g) by Heating

Temperature	Loss on heating in %	Number of molecules of H_2O lost
75	0.07	
85	0.13	
95	1.13	
105	1.44	
115	2.14	1 (5.90%)
145	13.72	2 (11.79%)
165	15.82	
205	18.39	3 (17.69%)
250	21.07	
300	22.91	4 (23.59%)

The stability of potassium tetraborate was also confirmed by keeping it for a year in hydrostats (Table 2).

If follows from the results given in Table 2 that potassium tetraborate tetrahydrate is stable under the most diverse storage conditions. Small changes in weight are obviously the result of condensation of water vapor on the crystal surfaces. It is interesting, in this connection, to compare potassium tetraborate with sodium carbonate and borax. The weight of sodium carbonate on standing in air of 50% relative humidity for 15 hours, increased by 0.3%. The weight of borax in air of 70% relative humidity did not change, but at a relative density of 3%, even large crystals of borax lost on an average 0.01% water in the course of 24 hours.

$K_2B_4O_7 \cdot 4H_2O$ dissolves readily in water. Its solubility increases rapidly with increasing temperature (Table 3).

Standardizing acid with potassium tetraborate. Establishment of the potentialities of potassium tetraborate as a base for standardizing acids was carried out by comparing titrations of ~ 0.1 N HCl carried out with this material, with those carried out with the aid of sodium carbonate and borax respectively. Sodium carbonate (chemically pure grade) was heated for 1 hour at 270-300° before use. Borax (analytical grade) was recrystallized twice and dried in a hydrostat with a relative humidity of 70% to constant weight.

TABLE 2
Change in Weight of $K_2B_4O_7 \cdot 4H_2O$ During Storage in the Course of One Year in Hydrostats

Preparation $K_2B_4O_7 \cdot 4H_2O$	Relative humidity in %	Wt. of preparation		Change in weight in %
		At beginning of storage	At end of storage	
Small crystals	3	2.6581	2.6584	+0.009
	30	1.9625	1.9624	−0.01
	50	1.8362	1.8366	+0.02
	70	2.1548	2.1557	+0.04
	90	1.9547	1.9570	+0.12
Large crystals	3	2.6284	2.6285	+0.003
	30	2.4115	2.4116	+0.004
	50	2.7111	2.7114	+0.01
	70	1.9899	1.9903	+0.02
	90	2.3862	2.3874	+0.05

TABLE 3
Solubility of $K_2B_4O_7 \cdot 4H_2O$ in Water*

Temperature	Solubility in g in 100 g water
0	8.8
15	15.3
20	18.5
25	21.9
35	30.2
50	46.5
60	58.6

---

* At various temperatures

Six titrations were carried out (in parallel) with each solution under identical conditions; 20 ml of each solution was taken using the same pipet every time. The equivalence point was established with the aid of standard solutions of Methyl Red. When sodium carbonate was used for titration, carbon dioxide was removed from solution just before the equivalence point by boiling the solution. Titration results are given in Table 4. The correctness of the results obtained when using potassium tetraborate was also checked by using individual aliquots (Table 5).

From Tables 4 and 5 it is clear that standarization by means of sodium carbonate, potassium tetraborate, and borax give results which are in good agreement. Even if these tests cannot be used as a basis for making a final decision whether potassium tetraborate gives completely reliable results, all the same they show definitely that these results are just as correct as those obtained with sodium carbonate and borax, and that potassium tetraborate can be used for standardizing acids.

TABLE 4

Titration of 0.1 N Solutions of Sodium Carbonate, Borax, and $K_2B_4O_7 \cdot 4H_2O$ Respectively with ~ 0.1 N HCl

0.1 N solution of the base in ml	Amt. of ~ 0.1 N HCl used in titration (ml) (mean of 6 runs)	Deviations in %
20.00 Na_2CO_3	19.96	} 0.15
20.00 $K_2B_4O_7 \cdot 4H_2O$	19.99	
20.00 $Na_2B_4O_7 \cdot 10H_2O$	19.99	0.00

All the properties of potassium tetraborate tetrahydrate show that this compound, undoubtedly, has advantages over other bases used in acidimetry. Potassium tetraborate which is readily obtained in a pure form, keeps in air without change for an indetermiate time. The amount of moisture in this compound under these conditions does not exceed 0.04%. For analysis, the accuracy of which does not exceed 0.1%, it can be used without preliminary drying or recrystallization.

The method of standardizing strong acids by means of potassium tetraborate is similar to that used for borax. Good results are obtained on titrating with 0.1 N HCl in the presence of Methyl Red or of a mixture of Methyl Red and Bromo Cresol Green. It is best to use a mixture of Methyl Red and Methyl Blue for standardizing dilute acids.

The rational equivalent weight of potassium tetraborate (d_{pycno} in bromobenzene at 25° = 1.941) is 152.70.

TABLE 5

Standaridization of ~ 0.1 N HCl Using Separate Aliquots of $K_2B_4O_7 \cdot 4H_2O$ and Borax, Respectively.

Series no.	Weight taken in g	Amount of ~0.1 N HCl used in ml	Normality of HCl	Mean normality of HCl
1	0.6539 $K_2B_4O_7 \cdot 4H_2O$	43.18	0.09918	0.09917
	0.6165 $K_2B_4O_7 \cdot 4H_2O$	40.73	0.09913	
	0.6237 $K_2B_4O_7 \cdot 4H_2O$	41.19	0.09920	
	0.6381 $K_2B_4O_7 \cdot 4H_2O$	42.13	0.09919	
	0.6301 $K_2B_4O_7 \cdot 4H_2O$	41.62	0.09914	
2	0.5929 $K_2B_4O_7 \cdot 4H_2O$	39.17	0.09912	0.09917
	0.6378 $K_2B_4O_7 \cdot 4H_2O$	42.13	0.09916	
	0.6454 $K_2B_4O_7 \cdot 4H_2O$	42.61	0.09919	
	0.6357 $K_2B_4O_7 \cdot 4H_2O$	41.99	0.09916	
	0.6581 $K_2B_4O_7 \cdot 4H_2O$	43.12	0.09920	
3	0.6233 $K_2B_4O_7 \cdot 4H_2O$	41.17	0.09917	0.09916
	0.6531 $K_2B_4O_7 \cdot 4H_2O$	43.12	0.09919	
	0.6509 $K_2B_4O_7 \cdot 4H_2O$	43.00	0.09913	
	0.6477 $K_2B_4O_7 \cdot 4H_2O$	42.78	0.00918	
	0.6258 $K_2B_4O_7 \cdot 4H_2O$	41.33	0.09915	
4	0.7034 $Na_2B_4O_7 \cdot 10H_2O$	37.22	0.09915	0.09918
	0.8058 $Na_2B_4O_7 \cdot 10H_2O$	42.61	0.09919	
	0.7950 $Na_2B_4O_7 \cdot 10H_2O$	42.05	0.09920	
	0.8153 $Na_2B_4O_7 \cdot 10H_2O$	43.11	0.09921	
	0.7690 $Na_2B_4O_7 \cdot 10H_2O$	40.67	0.09918	
	0.7829 $Na_2B_4O_7 \cdot 10H_2O$	41.41	0.09917	
5	0.8030 $Na_2B_4O_7 \cdot 10H_2O$	42.47	0.09916	0.09916
	0 8056 $Na_2B_4O_7 \cdot 10H_2O$	42.61	0.09917	
	0.7920 $Na_2B_4O_7 \cdot 10H_2O$	41.90	0.09915	
	0.8136 $Na_2B_4O_7 \cdot 10H_2O$	43.03	0.09916	
	0.7580 $Na_2B_4O_7 \cdot 10H_2O$	40.09	0.09918	
	0.7778 $Na_2B_4O_7 \cdot 10H_2O$	41.17	0.09913	

In conclusion, the authors would like to thank A. F. Ievina for valuable advice in planning the work.

SUMMARY

1. Potassium tetraborate $K_2B_4O_7$ $4H_2O$ is put forward as a primary standard for standarizing strong acids.

2. The properties of potassium tetraborate as a primary standard have been studied, and its advantages over sodium carbonate and borax demonstrated.

LITERATURE CITED

[1] A. T. Nutten., Metallurgia. 41, 111 (1949).

[2] A. Atterberg, Z. anorg. Chem. 48, 367 (1906).

[3] M. Dukelsky, Z. anorg. Chem. 50, 38 (1906).

[4] A. Ferrari and A. Magnani, Gazz. chim. ital. 69, 275 (1939).

Received February 1, 1956

SPECTROPHOTOMETRIC STUDY OF AQUEOUS SOLUTIONS OF QUINQUEVALENT VANADIUM

Yu. V. Morachevsky and L. I. Belyaeva

The A. A. Zhdanov Leningrad State University

More than 50 years of study of the state of quinquevalent vanadium in aqueous solution has not led to a unanimous opinion about the nature and conditions of existence of the fairly numerous forms of the ions of this element. The only generally accepted fact is that quinquevalent vanadium is amphoteric; in nature it is found as salts of vanadic acid, i.e. in the form of an anion, and only on lowering the pH considerably (below 1), is it possible to convert vanadium into a cation. On the form of V^V cations there is no serious disagreement. Most authors assume that the first form is V_2^+, while in more acid solutions VO^{3+} is formed [2, 3,10,11,12,13].

There is considerably more disagreement when it comes to the forms in which "acid" vanadates exist; the the overwhelming amount of work devoted to the study of quinquevalent vanadium relate to these "acid" vanadates [1,2,4,5,6,7,9,10,11,12 etc.].

All forms of the quinquevalent vanadium anion can be divided into ortho-, pyro-, and metavanadates. The close similarity between them and the corresponding phosphates gives a basis for searching for new analogies, but this cannot meet the objection that the reason for changes in the vanadates should be sought for, not in the extent of condensation, as is the case with phosphorus, but in the amphotericity of quinquevalent vanadium [2,6,11].

The changes which occur in vanadium solutions during acidification are readily observed by the naked eye. Addition of the first few drops of acid to an alkaline solution of vanadate leads to local orange coloration which does not disappear for a fairly long time, even on vigorous shaking.

When sufficient acid is added to neutralize excess alkali completely, the color assumes a stable character, and on further acidification, $V_2O_5 \cdot aq$. which is most often called vanadic acid, but is sometimes called hydrated oxide is precipitated. Further lowering of pH leads to solution of the precipitate which separated out earlier, and the vanadium is converted into a cation.

This series of transitions can be expressed schematically as follows:

VO_4^{3-}	$\rightarrow$	$V_2O_7^{4-}$	$\rightarrow$	VO_3^-	$\rightarrow$	$V_6O_{17}^{4-}$	$\rightarrow$	$V_2O_5 \cdot aq \downarrow$	$\rightarrow$	$VO_2^+ \rightarrow VO^{3+}$
ortho		pyro or dimer		meta or trimeta		hexa(also tetra penta, and dodeca)		precipitate of vanadic acid		

All investigators agree on the existence of the monomeric form of orthovanadate in strongly alkaline media.

With regard to the pyro- and meta forms, the argument is centered in the degree of association: the existence of mono- and dimers is assumed for pyrovanadate, and mono- and trimers for metavanadate.

Most disagreement centers on the polyvanadates. Almost all investigators are in agreement about the separation of vanadic acid in the precipitate.

Discrepanices arise not only between different authors, but even in the work of the same author carried out at different times [5,7]. Such disagreements cannot simply be related to experimental errors or method inaccuracies. Reference to insufficient purity of the original material is not convincing since, presumably, depending on conditions, there may exist very different forms of the anion of quinquevalent vanadium.

It is sufficient to adduce the far from complete list of existing zinc vanadates, so as to get an idea of the large variety of these compounds, and of the relatively small differences in composition between individual representatives of this series of salts [18]:

$$ZnV_2O_4;\ ZnV_2O_6;\ ZnV_4O_{11};\ Zn_2V_6O_{17};\ Zn_3V_2O_8;\ Zn_3V_4O_{16};\ Zn_6V_2O_{11};\ Zn_7V_6O_{27}.$$

Apparently, even small changes in the conditions used for isolating these compounds are sufficient to alter the state of the vanadium ion, or more accurately, to change the ratio between its individual forms. In our opinion, the reason for these disagreements is the striving of investigators to reduce all the varieties in which quinquevalent vanadium exists in aqueous solution, to a few principal forms, disregarding in doing so, the possibility of formation of intermediates. One of the main reasons for this large variety of forms is the large tendency of vanadium to associate; this tendency, naturally, increases with increasing concentration. On the basis of the work of Richardson and his coworkers [14], who studied polymerization of silicic acid in relation to its concentration, it may be reckoned that at room temperature, polymerization does not occur at concentrations less than $7\cdot10^{-5}$ g-atom/l. Most of the work on vanadium has been carried out in the range $n\cdot10^{-3}$ to $n\cdot10^{-1}$M, i.e. in conditions where association is known to take place. In trying to exclude the effect of the ionic strength of the solution on the properties and composition of the test ion, many authors have resorted to creating a constant salt background (~ 1-2 M Na_2SO_4 or NaCl), which of itself, cuts down on the amount of free solvent, i.e. it increases considerably the vanadium concentration [17].

Taking into account what has been said above, we set ourselves the problem of checking the effect of various factors on the state of quinquevalent vanadium ions, at concentrations which permit the existence of only the mono form. Observations of any changes which occur were made spectrophotometrically.

Doubly recrystallized ammonium vanadate was used for the work.

According to the results of Britton and Robinson [15], a 0.0833 N solution of orthovanadate hydrolyzes to the extent of 49%; accordingly we assumed that in ammonium vanadate solutions with concentrations of ~ $10^{-5}-10^{-4}$ g-atom/l; hydrolysis is complete.

Measurment of the optical density of aqueous solutions of ammonium vanadate, on increase of the concentration of the latter, showed the presence of at least two types of ions in solution (Fig. 1). In the concentration range $5\cdot10^{-5}-2\cdot10^{-4}$ g-atom/l, all points lie on a straight line, which on further increase of the vanadium concentration to $2\cdot10^{-4}$g-atom/l, changes its slope suddenly.

In line with the conclusions of Richardson and coworkers, on the first part of the graph we are dealing with the monomeric form of vanadic acid, while on the second part we are dealing with the associated form. The pH changes here from 5.9-6.2, i.e. very little.

On going from neutral media to more alkaline media (Fig. 2) one can distinguish two regions corresponding to two different forms of the quinquevalent vanadium ion. It is generally accepted that in strongly alkaline media the vanadium is in the form of the orthovanadate. It is clear from Fig. 2 that at vanadium concentrations up to $5\cdot10^{-4}$ g-atom/l, the change over to the orthovanadate is realized, starting at $1\cdot10^{-1}$ N NaOH. In the concentration range $10^{-3}-10^{-1}$ N NaOH, vanadium is apparently in the form of the ion $V_2O_7^{4-}$ Further lowering of the alkali content sharply depresses the amount of this form in solution and leads to the beginning of a new form (10^{-5}N NaOH – 10^{-5} N HCl)– the metavanadate.

On acidifying the solution (Fig. 3) it is again possible to distinguish at least two forms of quinquevalent vanadium.

Starting at an acid concentration of 10^{-5} N, and then further up to 10^{-2} N, there is clearly discernible a region of enhanced optical density of the solution (vanadium concentration $1.8\cdot10^{-4}$ g-atom/l); subsequently it falls to a value which is somewhat lower than that in the neutral region. A new and sharp increase in optical density starts when acid concentration reaches 10 N. According to published results, in $10^{-2}-10$ N acid, vanadium is in the form of a cation. According to Syrokomsky [13], the most simple relationship of the

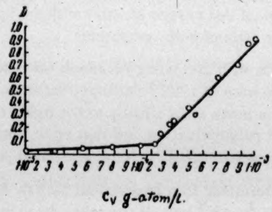


Fig. 1. Optical density of ammonium vanadate solutions in relation to concentration (λ = 300 mμ; d = 1 cm).

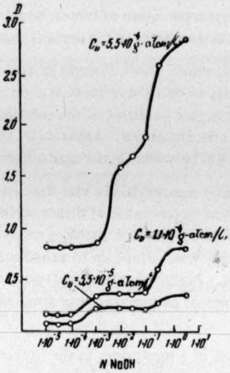


Fig. 2. Optical density of solutions of quinquevalent vanadium at different alkali concentrations (λ = 300 mμ; d = 1 cm).

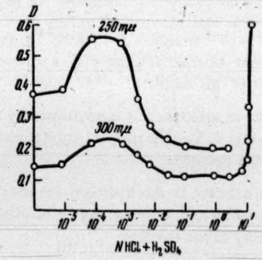


Fig. 3. Optical density of solutions of quinquevalent vanadium at different acid concentrations (C_V = = $1.84 \cdot 10^{-4}$ g-atom/l d = 1 cm).

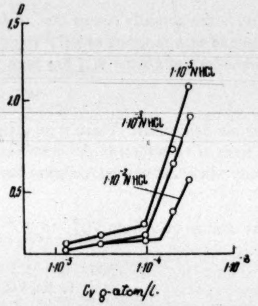


Fig. 4. Optical density of acidified solutions of ammonium vanadate (λ = 250 mμ; d = 1 cm).

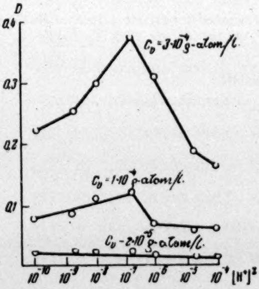


Fig. 5. Optical density of quinquevalent vanadium solutions, as a function of $[H^+]^2$ (λ = 300 mμ; d = = 1 cm).

oxidation-reduction potential V^V/V^{IV}, testifying to the form of the cation VO^{3+}, is observed under conditions where acid concentration is appreciable. It is recommended that vanadometric titration should be carried out in 10 N H_2SO_4. This may be arbitrarily taken as serving as an indirect indication that vanadium is in form of VO_2^+ in 10^{-2} – 10 N acid, and in the form VO^{3+} in more acid media. In the concentration range 10^{-5} N HCl to 10^{-5} N NaOH, vanadium exists in the form of the anion $(VO_3)_n^{n-}$. At the low vanadium concentrations with which we are dealing (< 10^{-4} g-atom/l, n was equal to 1.

Most disagreement centers on the concentration range of 10^{-5} – 10^{-2} N acid, in which vanadic acid is found in the most diverse forms from tetra- to dodecavanadic acid.

In order to clarify the nature of this maximum we checked on the relation between its magnitude and character and the vanadium concentration. Since a change in the form of vanadium is connected with a decrease in the amount of oxygen per atom of metal, which is caused by combination of this oxygen as water with the hydrogen ions in solution, the character of the over-all process should depend on the ratio of both components.

From Fig. 4, which shows changes in optical densities of the solution with increasing vanadium concentration, it is clear that on this curve there is a break at a vanadium concentration of $1 \cdot 10^{-4}$ g-atom/l, for an acidity up to $1 \cdot 10^{-3}$ N; at higher acidities of the solution ($5 \cdot 10^{-3}$ and $1 \cdot 10^{-2}$ N) the break shifts slightly to the right–towards higher vanadium concentrations. Apparently, the break indicates start of polymerization, and that up to vanadium concentrations of 10^{-4} g-atom/l the mono form exists, while at higher concentrations it is the associated product.

Our hypothesis is more likely, viz. that association processes are determined to a large extent by Van der Waals forces which become appreciable at distances between the particles of $10^{-7} - 10^{-8}$ cm. If one takes the diameter of VO_3^- to be 3.4 A (diameter $2r = 3.4$ A; $r = r_V + r_0 = 1.7$ A), then at $C_V = 10^{-4}$ g-atom/l the distance between particles is $\sim 7 \cdot 10^{-6}$ cm. Thus, up to vanadium concentration of 10^{-4} g-atom/l, one would expect only the mono form to be present. Published results, relating to higher vanadium concentrations, fall within the region where there are different degrees of polymerization–from which emerge the discrepancies between the results of different investigators.

The presence of a maximum in the optical density in the range $10^{-5} - 10^{-2}$ N acid ($C_V = 1.8 \cdot 10^{-4}$ g-atom/l) may be considered as the result of formation of some intermediate compound between VO_3^- and VO_2^+, a solution of which exhibits a higher light absorption than the original and final products of this transition.

The most natural assumption to make is that salts of VO_2VO_3-aq. exist in solution; this is confirmed by composition of the precipitate formed. This assumption is in agreement with what B. V. Nekrasov has pointed out [16], viz. that during electrolysis V_2O_5 partly goes to the anode, and partly to the cathode.

If salt formation actually occurs here, then the optical density of the solution in this hydrogen ion concentration range should be a function of $[H^+]^2$ (for constant vanadium concentration) and passes through a maximum at that point when half of all the VO_3^- has been converted into VO_2^+ according to the reaction:

$$VO_3^- + 2H^+ \rightleftharpoons VO_2^+ + H_2O.$$

Fig. 5 confirms our hypothesis. There is no sharp jump from vanadium as anion to vanadium as cation. The transition from one form of vanadium to the other occurs as a result of a gradual accumulation of the new form within the old, and only when this process has gone beyond the half-way stage is it possible to state that a new form is present.

Thus, the change over from VO_4^{3-} to VO^{3+} can apparently be represented schematically as a series of stages:

$$1.\ Na_3VO_4 + 2H_2O \rightleftharpoons NaH_2VO_4 + 2NaOH$$

$$2.\ \begin{array}{c} NaH_2VO_4 \rightleftharpoons NaHVO_3^+ + OH^- \\ NaH_2VO_4 \rightleftharpoons NaHVO_4^- + H^+ \\ \hline 2NaH_2VO_4 \rightleftharpoons Na_2H_2V_2O_7 + H_2O \end{array}$$

$$3.\ Na_2H_2V_2O_7 \rightleftharpoons 2NaVO_3 + H_2O$$

$$\text{or} \quad Na_2H_2V_2O_7 = NaHVO_3 - VO_4HNa \rightleftharpoons H^+ + OH^- + 2NaVO_3$$

$$4.\ NaVO_3 + H_2O \rightleftharpoons NaOH + HVO_3 \quad \text{or} \quad NaVO_3 + HCl \rightleftharpoons NaCl + HVO_3$$

$$5.\ \begin{array}{c} HVO_3 \rightleftharpoons H^+ + VO_3^- \\ HVO_3 \rightleftharpoons OH^- + VO_2^+ \\ \hline 2HVO_3 \rightleftharpoons H_2O + VO_2VO_3 \end{array}$$

$$6.\ VO_2VO_3 + 2HCl \rightleftharpoons 2VO_2Cl + H_2O$$

$$7.\ VO_2Cl + 2HCl \rightleftharpoons VOCl_3 + H_2O.$$

Reaction 1 occurs in alkaline medium at NaOH concentration of $5 \cdot 10^{-1} - 1 \cdot 10^{-1}$ N. When the ratio $[OH^+]:[V]$ becomes $\sim 100:1$, Reaction 2 predominates. An appreciable change to Reaction 3 only occurs when the vanadium concentration becomes greater than OH^- concentration. Reactions 3 and 4 give VO_3, accordingly, the optical density does not change from 10^{-5} N NaOH to 10^{-5} N HCl. Reaction 5 becomes appreciable at ratios of $[V]:[H^+]$, of about 1:1; and at a hundredfold excess of $[H^+]$ with respect to vanadium, reaction 6 is completely finished. Reaction 7 apparently, occurs at appreciably high concentrations of $[H^+]$ in very strong acid media.

SUMMARY

1. Aqueous solutions of quinquevalent vanadium compounds have been studied spectrophotometrically in a wide hydrogen ion concentration range (from 6.0 N NaOH to 10 N H_2SO_4).

2. It has been shown that in the region near the isoelectric point (pH ~ 2) a vanadic salt of vanadium $VO_2VO_3 \cdot aq.$, is formed. The polyvanadic acids discovered by other research workers should be regarded as association products of molecules of this salt.

3. It has been shown that polymerization of vanadium (5) in aqueous solution starts at a concentration of 10^{-4} g-atom/l; this explains the discrepanices between results of different investigators, who carried out their studies under conditions of appreciably higher concentrations ($> 10^{-3}$ M).

4. Possible schemes for transitions between individual forms of quinquevalent vanadium ions in aqueous solutions have been put forward.

Received April 12, 1956

LITERATURE CITED

[1] Dullberg, Z. physik. Chem. 45, 129 (1903).

[2] P. Souchay and G. Carpeni, Bull. soc. chim. France 160 (1946).

[3] A. B. Hart and J. R. Partington, J. Chem. Soc. 1940, p. 1532.

[4] A. V. Dumansky, J. Russ. Phys. Chem. Soc. 54, 8, 703 (1924).

[5] G. Jander and T. Aden, Z. physik. Chem. 144A, 197-212 (October, 1929).

[6] L. P. Ducret, Ann. chim. (Paris) 6, 705 (1951).

[7] K. F. Jahr and G. Jander, Z. anorg. Chem. 220, 201, 27, 10 (1934).

[8] H. Brintzinger and G. Wallach, Z. anorg. Chem. 224, 103 (1935).

[9] I. I. Mikhailenko and K. G. Shveiblit, Rare Metals 4, 3, 19-27 (1934).

[10] H. T. S. Britton and G. Welford, J. Chem. Soc. 1940, 764.

[11] H. T. Britton and R. A. Robinson, J. Chem. Soc. 1930, 1261.

[12] H. T. S. Britton and G. Welford, J. Chem. Soc. 1940, 895.

[13] V. S. Syrokomsky and Yu. V. Klimenko, Vanadimetry (Metallurgical Press, 1950), pp. 15-17.

[14] E. Richardson and J. A. Waddams, Research 7, 7, 542 (1954).

[15] H. T. S. Britton and R. A. Robinson, J. Chem. Soc. 1932, p. 1955.

[16] B. V. Nekrasov, Course of General Chemistry (State Chem. Press, 1952), p. 416.

[17] G. Harned and B. Owen, Physical Chemistry of Solutions of Electrolytes (Foreign Lit. Press, 1952), p. 575.

[18] Chemical Abstracts 20, 1185; 34, 982^5; 36, 1561^8; 48, 1837 h. g; 49, 8247 f.

BLANK
PAGE

ELECTROCHEMICAL BEHAVIOR OF ELECTRODES DURING POTENTIOMETRIC TITRATION WITH TRILON B

B. N. Kabanov and L. Ya. Polyak

Up to recently organic complexing agents and precipitants have not been used in potentiometric analysis because of the absence of indicator electrodes suitable for this purpose. The first article on the application of Trilon B (Complexone III) in potentiometric analysis was published by Pribil [1], who titrated a number of elements in a weakly acid medium buffered by ammonium acetate. The mechanism of the potentiometric titration in weakly acid and neutral solutions (at pH from 1 to 7), given by the author in the cited article, is based on the theory of oxidation-reduction titration. The author begins with the premise that in the case of cations which exist, e.g., in di- and trivalent forms, there is always observed a difference in stability of the complexes MeY^{2-} and MeY^-, where Y^- is the complexing anion. In view of this, in an oxidation-reduction system, in the presence of Trilon B, the potential of the indicator platinum electrode is determined by the equation:

$$\varepsilon = \varepsilon_0 + 0.059 \log \frac{K_1}{K_2} + 0.059 \log \frac{[MeY^-]}{[MeY^{2-}]},$$

where K_1 and K_2 are the respective instability constants of the complexes MeY^- and MeY^{2-}.

During titration of such a system with a solution containing a complexing anion, the potential change is similar to that observed during normal redox titration.

This appears to be a prerequisite for direct potentiometric titration of cations possessing two valency states (e.g., $Fe^{3+} \mid Fe^{2+}$; $Cu^{2+} \mid Cu$; $Cr^{3+} \mid Cr^{2+}$, etc.).

If the solution contains cations of a metal which does not exhibit variable valency (e.g., Zn^{2+}, Ni^{2+}, Cd^{2+}), then in order to determine such cations Pribil suggests creating an oxidation-reduction system by back titration of excess Trilon B with ferric chloride,* since Fe^{3+} and Fe^{2+} ions form complexes of varying stability with Trilon B. This method of titration permits the use of platinum as indicator electrode.

The method of titration proposed by Pribil can be successfully used only for direct and back titration of those elements which form stable complexes with Trilon B in weakly acid and neutral media, at pH 1-7 (Ni, Cd, Zn, Cu, Fe, etc.). For elements such as Ba, Ca, and Mg, which do not form complexes with Trilon B in acid solution, but give stable complexes in ammoniacal media at pH of 10-12, titration by Pribil's method is impossible.

No published references could be found on the possibility of carrying out a potentiometric titration of such elements with Trilon B. One of the authors of the present article recently developed a potentiometric method for determination of small amounts of barium in heat resistant alloys based on nickel, in which Trilon B was used. The method was based on dissolving the precipitate of barium sulfate in an ammoniacal solution of Trilon B, followed by back potentiometric titration of excess unreacted Trilon B with barium chloride [2]. In this connection it was of interest to study the mechanism of electrode processes which occur during titration of barium and other cations in ammoniacal media with Trilon B.

EXPERIMENTAL

In order to choose an indicator electrode for potentiometric titration of barium and other cations in ammoniacal media with Trilon B, we measured the electrode potentials of a few metals in ammoniacal solutions at various Trilon B concentrations (Table 1).

---

* Ferric chloride solution invariably contains a small amount of ferrous ions.

TABLE 1

Electrode Potentials of Various Metals in Ammoniacal Solutions with Respect to the Saturated Calomel Electrode (in mv)

	W	Cr	Mo	Al	Sb	Pt
$NH_4OH + NH_4Cl$ [1]	—435	—240	—375	—520	—550	—25
[1] + 0,0001 *N* Trilon B	— 490	—240	—405	—520	—550	—20
[1] + 0,001 *N* Trilon B	—500	— 240	—405	—525	—545	—20
[1] + 0,01 *N* Trilon B	—505	— 220	—405	—520	—540	—20

If follows from these results given in Table 1 that: 1) a platinum electrode in ammoniacal solution does not act as an indicator electrode (during titration with Trilon B); 2) of the electrodes tested, only tungsten and molybdenum can be used as indicator electrodes; 3) a potential shift of the tungsten and molybdenum electrodes is observed on addition of very small amounts of Trilon B (0.0001 N). Further increases in Trilon B concentration have practically no effect on the potential of the tungsten electrode.

The reproducibility of the potentials of the chromium, aluminum, and antimony electrodes is poor. Only the potentials of platinum, tungsten, and molybdenum are well reproduced in ammoniacal solutions of Trilon B.

It is thus possible to conclude that during direct and back potentiometric titration of elements in ammoniacal solutions of Trilon B, with a bimetallic pair platinum – tungsten, the indicator electrode will be tungsten, and the reference electrode platinum.

It has been established previously that it is possible to use a bimetallic electrode pair composed of Pt – W for many oxidation-reduction reactions in which the platinum electrode always plays the part of the indicator electrode, while the tungsten plays the part of reference electrode [3]. Now, during titration of ammoniacal solutions of Trilon B, we come across a rare case, when it is the tungsten electrode which acts as the indicator electrode.

In order to establish how the platinum and tungsten electrodes behave during titration, a series of experiments were carried out on compensation titration of barium chloride solutions (0.01 N) with Trilon B (0.01 N) and back titration of Trilon B with barium chloride, in which the following electrode pairs were used for titration: 1) Pt – W; 2) W – calomel electrode; 3) Pt – calomel electrode.

Titration curves are shown on Figs. 1,2,3 and 4. The curves show that during titration of barium ions with Trilon B, the potential of the platinum electrode remains unchanged (Fig. 3), while that of the tungsten electrode changes sharply at the equivalence point (Fig. 2). Accordingly, titration in ammoniacal media with the pair Pt – W, is analogous to titration with the pair W – calomel half element (Figs. 1 and 2).

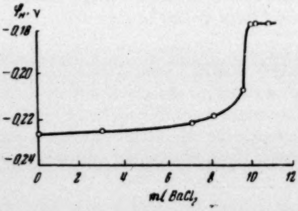


Fig. 1. Potentiometric titration of 0.01 N Trilon B with 0.01 N barium chloride using the electrode pair Pt – W.

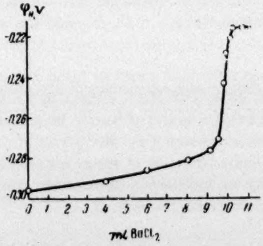


Fig. 2. Potentiometric titration of 0.01 N Trilon B with with 0.01 N barium chloride using the pair W – calomel half element.

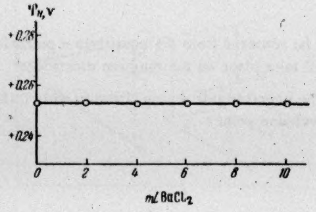


Fig. 3. Potentiometric titration of 0.01 N Trilon B with 0.01 N barium chloride using the pair Pt – calomel half element.

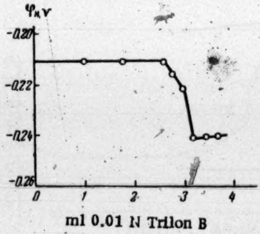


Fig. 4. Potentiometric titration of barium chloride with 0.01 N Trilon B, using the pair W – calomel half element.

To find an answer to the question what causes the shift in potential of the tungsten electrode to the negative side during titration with Trilon B, it is necessary to find out what are the electrochemical processes which determine the potential of the tungsten electrode.

The potential of an electrode is determined by two electrochemical processes – cathodic and anodic. For reversible metallic electrodes, these processes consist in the exchange of metal ions between electrode and solution. In the case of irreversible electrodes, the anode process usually consists of dissolving of the metal, while the cathode process consists of deposition of hydrogen on it, or of ionization of oxygen [4].

In order to establish the nature of the anode and cathode reactions which occur on the tungsten electrode, we calculated the potentials of air, hydrogen, and tungsten electrodes in ammoniacal solutions with pH 10 relative to the normal hydrogen electrode.

1. Potential of the reversible hydrogen electrode at pH 10

$$\varepsilon = \varepsilon_0 + 0.059 \log a_{H^+}, \quad -\log a_{H^+} = pH = 10;$$
$$\varepsilon = 0 - 0.059 \cdot 10 = -0.59\,v.$$

2. Potential of a stationary air electrode at pH 10 (approximately

$$\varepsilon_{O_2} = \varepsilon_0 + 0.059 \log a_{H^+},$$
$$\varepsilon_{O_2} = 0.85 - 0.059 \cdot 10 = +0.26\,v.$$

3. Theoretical equilibrium potential of the tungsten electrode, determining the reaction

$$W + 8OH^- = WO_4^{2-} + 4H_2O + 6\,v$$

v at pH 10 has the value

$$\varepsilon = \varepsilon_0 - \frac{0.059}{6} \log\log a_{OH^-}^{8} + \frac{0.059}{6} \log a_{WO_4^{2-}};$$

$$\varepsilon_0 = -1.1\,v: \quad \text{let} \quad [WO_4^{2-}] \approx 10^{-4};$$

$$\varepsilon = -1.1 - \frac{0.059 \cdot 8}{6} \log 10^{-4} + \frac{0.059}{6} \log 10^{-4} = -0,82\,v.$$

Calculated and experimental results are given in Table 2.

The experimentally measured potential of the tungsten electrode in ammonia (–0.2 v) is considerably more positive than the equilibrium of the tungsten electrode in ammonia at pH 10 (–0.82 v) (if it is assumed that it is determined by the reaction given above), i.e. the tungsten is partly passive in ammonia solutions (its potential is shifted towards the positive side as a result of its oxidation by atmospheric oxygen).

The stationary potential of the tungsten electrode in ammonia (–0.2 v) lies between the potentials of the tungsten and air electrodes in ammonia; this indicates that the stationary potential of the tungsten electrode is determined by oxidation processes of tungsten on the one hand, and reduction of oxygen on the other.

Graphically the process of tungsten oxidation is expressed by the anode polarization curve, while reduction of oxygen is represented by the cathodic polarization curve. The intersection point of the extrapolated curves (cathodic and anodic) gives the value of the experimentally measured stationary potential of the tungsten electrode in the given solution.

This can be depicted by the scheme shown in Fig. 5.

Since the potential region in which titration is carried out is far removed from the equilibrium potentials of the tungsten and air electrodes, then only these two processes will take place on the tungsten electrode.

How can one explain the shift in the stationary potential to the negative side during titration with Trilon B, in other words what causes the potential jump observed at the equivalence point ?

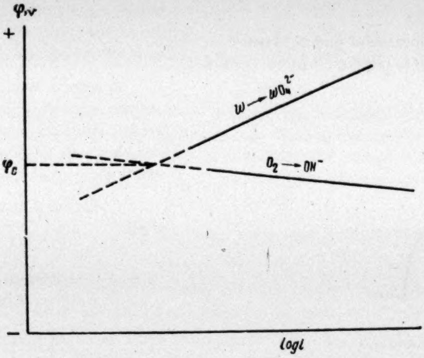


Fig. 5. Scheme for the establishment of the stationary potential on the tungsten electrode.

TABLE 2

Potentials of the Air, Tungsten, and Hydrogen Electrodes in Ammoniacal Media with Respect to the Normal Hydrogen Electrode (at pH 10)

1) Potential of the air electrode.	$\epsilon \approx +0.26$ v
2) Experimental potential of the tungsten electrode.	$\epsilon = -0.20$ v
3) Experimental potential of the tungsten electrode in the presence of Trilon B.	$\epsilon = -0.23$ v
4) Reversible potential of the hydrogen electrode.	$\epsilon = -0.59$ v
5) Equilibrium potential of the W-electrode (against WO_4^{2-}).	$\epsilon = -0.82$ v

There are three possibilities. The stationary potential is displaced to the negative side: either because of the slowing down of the cathode process, the speeding up of the anode process, or because of both processes simultaneously. This can be represented graphically as shown in Fig. 6.

Thus, the answer to the problem we are interested in can be found by analyzing the polarization curves for the tungsten electrode taken in ammoniacal buffer solutions in the presence and absence of Trilon B. From the change in shape of the cathodic and anodic curves under the influence of Trilon B, we hoped to establish which of the processes determining the stationary potential of the tungsten electrode in ammoniacal solution is affected by the Trilon B, and consequently find out why the stationary potential is shifted towards the negative side.

We took polarization curves (cathodic and anodic) in buffered ammoniacal solutions ($NH_4OH + NH_4Cl$) with and without Trilon B, respectively. The method used for taking polarization curves has been described before [5].

Polarization curves taken while the solution was mechanically agitated (in the same way as was used for

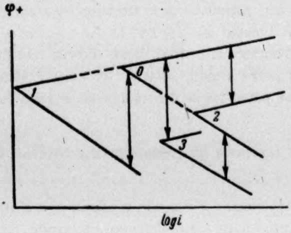


Fig. 6. Scheme for shift in stationary potential (the ciphers in the diagram refer to the three cases described in the text)

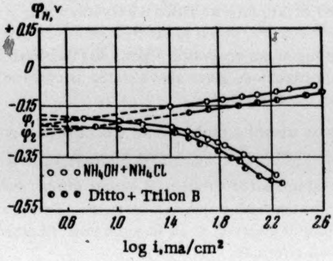


Fig. 7. Polarization curves of a tungsten electrode in an ammoniacal medium.

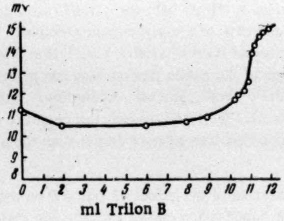


Fig. 8. Potentiometric non-compensated titration of 0.01 N barium chloride with 0.01 N Trilon B using the pair Mo – calomel half element.

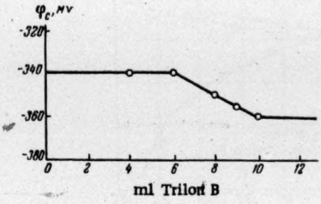


Fig. 9. Potentiometric compensated titration of barium chloride with Trilon B, using the pair Mo – calomel half element.

taking potentiometric titration curves) are shown in Fig. 7. As Fig. 7 shows, Trilon B affects both processes: it speeds up the process of anodic dissolving of tungsten (it lowers the overvoltage of the anodic process) and slows down the ionization of oxygen (increases the overvoltage of the cathodic process). As a result of this effect of Trilon B on the electrode processes, the stationary potential of the tungsten electrode is displaced to the negative side ($\Delta\varphi = \varphi_2 - \varphi_1$). According to this, during compensation titration with Trilon B, the potential jump occurs as a result of the effect of Trilon B on both the processes which determine the potential of the tungsten electrode.

Non-compensated titration consists of connecting the two electrodes to the poles of a sensitive galvanometer (millivoltmeter) through a high ohmic resistance. During titration one follows directly on the millivoltmeter scale changes which occur in the current flowing through the given element. The equivalence point is taken as that point where there is a sharp change in current.

Since the potential of the tungsten electrode is more negative than that of the platinum one, then during non-compensated titration with a pair including a platinum electrode, the tungsten electrode is polarized anodically. Therefore, for characterizing the behavior of an electrode during non-compensated titration, the anodic polarization curve and those processes which determine its displacement are of significance.

During non-compensated titration with Trilon B, the potential jump occurs as the result of a lowering of the overvoltage of the anodic process, i.e., acceleration of the rate at which tungsten dissolves. It could be postulated that the molecules of Trilon adsorbed by tungsten, drive out the oxygen from the surface of the electrode and activate it. Activation is expressed by a shift in potential to the negative side.

In order to find out how the passage of the current through the tungsten electrode during non-compensated titration affects the value of potential change near the equivalence point, potentiometric titration by a compensation method of barium with Trilon B was carried out, but a small anode current was applied to the electrodes ($i = 2.5 \cdot 10^{-5}$ A/cm^2), which passes through the circuit during non-compensated titration. Tests showed that the potential jump at the equivalence point has the same value as the shift in the anodic polarization curve. This confirms our hypothesis given above on the mechanism of the shift in the potential at the equivalence point during non-compensated titration.

We also studied a molybdenum electrode as a potential indicator electrode for potentiometric titration of cations in ammoniacal solution with Trilon B.

Non-compensated titration of barium (direct and back) with a molybdenum electrode proceeds in a similar fashion to titration with a tungsten electrode. During compensated titration with a molybdenum electrode, no potential jump is observed at all in some tests; in others it is very small (of the order to 5-10 mv instead of 30 mv for a tungsten electrode, Figs. 8, 9).

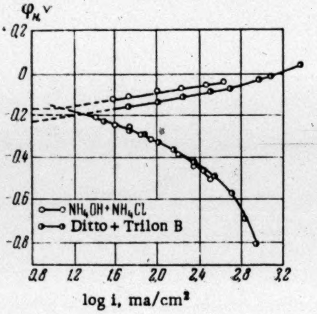


Fig. 10. Polarization curves for a molybdenum electrode in an ammoniacal medium.

Polarization curves of a molybdenum electrode, taken in air during mechanical agitation of the solution (Fig. 10), differ from the corresponding curves for a tungsten electrode. While in the case of a tungsten electrode Trilon B affects both the cathodic and anodic processes, in the case of a molybdenum electrode we observed a different state of affairs, viz., Trilon B lowers the overvoltage of the anode process, and has practically no effect on the cathode process. Accordingly, the stationary potential is shifted toward the negative side on addition of Trilon B to a lesser extent than the anode potential.

This character of the effect of Trilon B on the position of the polarization curves explains the reason for the fact that non-compensated titration, in the course of which the molybdenum electrode paired with a platinum electrode is polarized anodically, proceeds with a more clearly defined potential jump at the equivalence point than in the case of compensated titration.

SUMMARY

1. A number of metals have been studied as potential electrodes for potentiometric non-compensated titration of elements in ammoniacal solutions with Trilon B. It has been established that tungsten and molybdenum electrodes can be used as indicator electrodes. A platinum electrode can be used as reference electrode in these cases.

2. An explanation has been given of the electrode processes which occur during potentiometric titration of such elements as barium, calcium, and magnesium which form stable complexes with Trilon B at pH>> 7.

3. On the basis of calculations and measurements of potentials, it has been established that the processes which determine the stationary potential of the tungsten electrode in ammoniacal solution, are oxidation of tungsten one the one hand, and reduction of oxygen on it, on the other.

4. Polarization curves have been taken for a tungsten electrode in ammoniacal solution both in the presence and in the absence, respectively, of Trilon B. It has been established that Trilon B affects both processes which determine the stationary potential of the tungsten electrode: it speeds up anodic dissolution of the tungsten and slows down ionization of oxygen on it.

5. During non-compensated titration using paired platinum and tungsten electrodes, the tungsten electrode is polarized anodically. Accordingly, the potential jump on the tungsten electrode during titration is determined by the effect of Trilon B on the anodic process alone. It can be postulated that molecules of Trilon B adsorbed on

the tungsten, drive out the oxygen from the electrode surface and activate it at the same time; as a consequence the potential is displaced towards the negative side.

6. The mechanism of the shift in the stationary potential of a molybdenum electrode caused by Trilon B is different from that of tungsten electrode: Trilon B lowers the overvoltage of the anodic process of molybdenum oxidation, and has no effect on the cathodic process of oxygen ionization.

LITERATURE CITED

[1] Pribil, Chem. Listy 10, 222 (1950).

[2] L. Ya. Polyak, J. Anal. Chem. (In Press).

[3] L. Ya. Polyak, Factory Lab. 19, 1041 (1953).

[4] A. N. Frumkin, V. S. Bagotsky, Z. A. Ioffa and B. N. Kabanov, Kinetics of Electrode Processes (Moscow State University Press, 1952), p. 284.

[5] L. Ya. Polyak and B. N. Kabanov, J. Anal. Chem. 8, 253 (1953) (T.p. 283).*

Received October 3, 1955

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

ORGANIC COPRECIPITANTS (COLLECTORS)

PART 7. COPRECIPITATION OF BISMUTH.* DETERMINATION OF SMALL AMOUNTS OF BISMUTH IN ALLOYS BASED ON Cr AND Ni

V. I. Kuznetsov and L. I. Papushina

For precipitation of small amounts of bismuth from large volumes, it has been recommended that use be made of a number of inorganic coprecipitants (collectors), including the hydroxides of iron or aluminum and some other materials, information about which can be found in Busev's monograph [1]. It is most convenient to coprecipitate bismuth with organic coprecipitants.

Bismuth, in the form of an iodide complex anion BiI_4^-, is quantitatively coprecipitated with a precipitate of methyl violet iodide (Table 1) even at dilutions of $1:1\cdot10^8$ (1γ bismuth in 100 ml volume) with simultaneous separation from a number of elements. The precipitate of methyl violet iodide is readily filtered, washed and ashed.

The selectivity of coprecipitation of bismuth is readily evaluated on the basis of considerations set forth in articles on the theoretical bases of the action of organic coprecipitants [2]. All those elements which, under the experimental conditions employed are present as heavy anions similar to BiI_4^- or form sparingly soluble iodides, are precipitated at the same time as bismuth. Many elements do not form such anions, and accordingly, coprecipitation with Methyl Violet is suitable for separation of very small amounts of bismuth from many elements. E.g., separation of bismuth from nickel and chromium goes very well, so that it is possible to use coprecipitation with Methyl Violet for determining very small amounts of bismuth in alloys based on chromium and nickel (See Table 1).

Copper, some antimony, and possibly tin are coprecipitated with bismuth; if, therefore, appreciable amounts of any of these elements are present, they must be removed.

TABLE 1

Precipitation of Bismuth from Pure Solutions and From Solutions Containing Nickel and Chromium (in all cases the volume of the original solution was 500 ml)

No. of experiment in order	Dilution of bismuth	Ni or Cr added	Ratio $\frac{Bi}{Ni+Cr}$	Bismuth	
				Added	Found
1	$1:1\cdot10^8$	—	—	5	4
2, 3	$1:2.5\cdot10^7$	—	—	20	20; 20
3, 4	Ditto	3,25 г $NiSO_4\cdot7H_2O$	1 : 32 000	20	18; 20
5, 6	" "	3,25 г $NiSO_4\cdot7H_2O$ 2,4 г $KCr(CO_4)_2\cdot12H_2O$	1 : 45 000	20	20; 23
7, 8	$1:1.2\cdot10^7$	—	—	40	40; 40
9, 12	$1:2.5\cdot10^7$	Solution of 2 g Cr—Ni steel	1 : ~100 000	20	20; 19 20; 20
13—16	Ditto	Solution of 4 g Cr—Ni steel	1 : ~ 20 0000	20	18; 20 20; 18

---

* Previous communications see: [2], and also J. Anal. Chem. 10, 32, 211 (1955) (C. B. Translation p. 197); J. Inorg. Chem. 1, 579 (1956); Use of Labelled Atoms in Analytical Chemistry, Collections of GEOKhI USSR Acad. Sci. Moscow, 1955, p. 24.

In the chrome-nickel steels normally met the content of antimony and tin is so small (~. 0.00X%) that can be ignored. Evaporation of the acid solution, as described in theprocedure given below to the inception of crystallization of the salts favors volatilization of part of the tin. Copper should be removed since it affects the subsequent colorimetric determination of bismuth. Copper may also come from the Methyl Violet, some types of which contain appreciable amounts of copper [3]. Preparations of Crystal Violet, particularly "indicator" grade, are purer in this respect. •

Below we described the technique we have worked out for determining small amounts of bismuth (0.005 - 0.0005%) in alloys based on chromium and nickel. The method consists of precipitating bismuth from 0.2 - 0.3 N sulfuric acid solution with a precipitate of methyl violet iodide after preliminary removal of silicon and some of the antimony. After ashing and dissolving the residue, bismuth is separated from copper by coprecipitation with aluminum hydroxide, and then colorimetrically determined as the iodide complex anion.

PROCEDURE

Reagents Required

1. An approximately 1% solution of Methyl Violet. Instead of following the published method for removing the copper contained in Methyl Violet by means of hydrogen sulfide [4], it is more convenient to proceed as follows. 11g of Methyl Violet is dissolved in 1000 ml of ~ 0.05 N hydrochloric acid, and with good stirring, 25-50 ml of a 5% solution of NH_4I or KI is added to the solution in a fine stream, in order to precipitate part of the Methyl Violet as the iodide. The whole is vigorously stirred for 1-2 hours and filtered twice through the same filter paper. For determination of bismuth in steels containing copper, there is no need to purify the Methyl Violet from copper.

2. A 5% aqueous solution of NH_4I or KI.

3. Wash solution. To 1000 ml of 0.2 N sulfuric acid is added 10-20 ml each of solutions 1 and 2. It can be used with without concern about formation of a precipitate.

4. Dilute sulfuric acid (1:4). To 80 ml water, 20 ml concentrated sulfuric acid is added.

5. Ammonia – aqueous solution.

6. Solution containing Al. 0.5 g of pure aluminum is dissolved in hydrochloric acid and the solution diluted with water to 100 ml.

Analytical Procedure

1-4 g of chrome-nickel steel turnings, depending on the amount of bismuth expected, is dissolved in a mixture of HCl and HNO_3 in a 500 ml beaker, and the solution evaporated until salts begin to crystallize out. It is then

TABLE 2

Determination of Bismuth in Chrome-Nickel Steels

Steel Sample	wt. of sample in g	Bismuth added in γ	Total bismuth content in %	Bismuth found	
				By the method described in %	By the hydrogen sulfide method [6] in %
I	1	0	—	0.0005; 0.0005	
I	1	50	0.0055	0.0045; 0.0040; 0.0049 0.004; 0.0046	0.0047
I	1	30	0.0035	0.0025; 0.0028; 0.0029; 0.0033; 0.0026; 0.0037	0.0031; 0.0032
II	2	0	—	0.00012; 0.00019; 0.00016; 0.00012	
II	2	20	0.00115	0.0010; 0.00098; 0.00098; 0.0011; 0.0009; 0.0013	0.00092; 0.0011
III	4	0	—	0.00006; 0.00004	
III	4	32	0.00085	0.00075; 0.00071; 0.00078; 0.00081; 0.00079	0.00088; 0.00094
III	4	20	0.00055	0.00046; 0.00050; 0.00052; 0.00053; 0.00050 0.00056; 0.00056; 0.00054; 0.00054	0.00054; 0.00050

• Crystal Violet is considerably less soluble than Methyl Violet.

cooled, 15-40 ml of concentrated sulfuric acid added, and the whole heated on a hot plate to the appearance of white fumes of sulfuric acid. It is cooled again, carefully diluted with 100-250 ml water and the mixture heated with stirring. After the salts have dissolved completely, the solution is left for 20 minutes, and the silicic acid filtered off on a double filter (white ribbon grade), the filtrate being collected in a 1 liter beaker. When 4 g of sample is taken, the bismuth is precipitated from a volume of 700 ml. When the sample weight is 2 g or less, precipitation is effected from 500 ml. Excess acid is neutralized with ammonia to a weak acid reaction to Congo paper, and immediately 3 ml of dilute sulfuric acid (1:4) added per 100 ml solution. Further, for each 100 ml solution is added 1-2 ml of NH_4I or KI, followed by 6-7 ml of Methyl Violet solution, and after this another lot of 20-18 ml of NH_4I or KI (in each case the volumes are per 100 ml of the solution) until formation of a good black precipitate of methyl violet iodide. The whole is mixed for 3 minutes and left for 1-2 hours or overnight. It is filtered through a paper filter (white filter), washed with wash solution, slightly dried on the funnel, transferred to a quartz crucible, moistened with a few drops of hydrochloric acid and sulfuric acid, and then carbonized on a hot plate. To ash it, it is heated in a muffle at a dark red heat until all carbon particles are completely removed. If the latter are hard to get rid of, the crucible is cooled again, a few drops of sulfuric and nitric acids added, and the whole heated to almost complete removal of sulfuric acid.

The residue is dissolved in hydrochloric acid, transferred to a small beaker, 1 ml of ammonium chloride solution is added, and then for removal of copper, the basic salt of bismuth is precipitated with ammonia simultaneously with aluminum hydroxide. The precipitate is filtered through a small filter, and the washed precipitate plus filter placed in a small beaker, and dissolved by heating in hydrochloric acid. The solution is again filtered through a small filter, the filter washed with hydrochloric acid, and 2.5 ml of dilute (1:4) sulfuric acid added; the hydrochloric acid is removed by evaporation, and then the solution is transferred to a 25 ml standard flask with water acidified with a few drops of sulfuric acid. Bismuth is determined colorimetrically by the usual method with potassium iodide and sulfurous acid [5], in an aliquot part of the solution thus obtained.

Results obtained during determination of bismuth (in chrome-nickel steels contaminated with bismuth) by means of the method described, and results obtained during determination of bismuth by means of the hydrogen sulfide method, are given in Table 2.

SUMMARY

During precipitation of the sparingly soluble iodide of Methyl Violet, quantitative removal of any bismuth contained in the solution, down to dilutions of $1:1 \cdot 10^8$, from the precipitate, occurs.

Nickel and chromium are not attracted into the precipitate. A method is described for determining small (0.00X - 0.000X%) amounts of bismuth in chrome-nickel steels, which is based on separation of bismuth by coprecipitation with methyl violet iodide, with subsequent colorimetric determination as the iodide complex.

Received February 3, 1955

LITERATURE CITED

[1] A. I. Busev, Analytical Chemistry of Bismuth (Acad. Sci. USSR Press), p. 24 ff.

[2] V. I. Kuznetsov, J. Anal. Chem. 9, 199 (1954)(T.p. 221)*; Session of the Acad. Sci. USSR on the Peaceful Uses of Atomic Energy, Chem. Sci. Section, (Moscow, 1955), p. 301.

[3] L. G. Landau and A. A. Gribov, Technology of Organic Dyes, (Moscow - Leningrad, 1934), p. 217.

[4] M. A. Popov, Factory Lab. 13, 1489 (1947).

[5] A. K. Babko and A. T. Pilipenko, Colorimetric Analysis (Moscow - Leningrad, 1951), p. 207.

[6] Z. S. Mukhina and I. A. Zhemchuzhnaya, New Methods of Chemical Analysis of Steels and Alloys (State Defense Press, 1952).

---

*T.p. = C. B. Translation pagination.

BLANK
PAGE

SOME PROPERTIES OF DI-β-NAPHTHYLTHIOCARBAZONE AND ITS BISMUTH AND NICKEL COMPLEXES

A. S. Grzhegorzhevsky

Dnepropetrovsk Metallurgical Institute

Absorption Curve of Di-β-naphthylthiocarbazone

Solutions of di-β-naphthylthiocarbazone in CCl_4, and also in $CHCl_3$ and $(CH_3)_2CO$ are colored green. The presence of the color determines the selectivity of absorption. The absorption curve for a $0.9 \cdot 10^{-5}$M solution of di-β-naphthylthiocarbazone in CCl_4 was taken in a FM- photometer with a layer thickness of 1 cm. The molarity of the solution of di-β-naphthylthiocarbazone was determined photocolorimetrically by comparison with solutions of known concentration. The absorption curve (Fig. 1) has two maxima: at 665 mμ and 465 mμ. The molar absorption coefficient is equal to 40,000. Solutions of dithizone in CCl_4 have maxima at 618 and 450 mμ [1,2], while the molar absorption coefficient is equal to ~ 15,000. Thus, the maxima for solutions of di-β-naphthylthiocarbazone in CCl_4 are shifted to the longer wave length side.

Dissociation Constant of Di-β-naphthylthiocarbazone

Di-β-naphthylthiocarbazone, as Suprunovich's experiments showed [3], is similar in a number of its properties to dithizone. Nevertheless, di-β-naphthylthiocarbazone is fairly sharply distinguished from dithizone with respect to aqueous solutions of alkali, sodium carbonate, and ammonia. Suprunovich established that di-β-naphthylthiocarbazone does not dissolve even in 10% alkali, while dithizone dissolves in dilute alkali solutions. In order to clarify the qualitative picture of the distribution of di-β-naphthylthiocarbazone between CCl_4 and the aqueous phase, the following experiments were carried out. Into a test tube with a ground-glass stopper was introduced 1 ml of a solution of di-β-naphthylthiocarbazone and 10 ml of a buffer solution of a known pH. The contents of the tube were shaken for 180 seconds. After allowing the layers to separate out, the color of the CCl_4 layer was compared visually with the color of the original solution of di-β-naphthylthiocarbazone. Even such a rough comparison as this enabled us to judge the behavior of di-β-naphthylthiocarbazone at varying pH. Thus, at pH up to 9.8, no appreciable change in the color of the CCl_4 layer was observed. At pH > 10, weakening of the color of the CCl_4 layer occurred while the aqueous layer acquired a pale yellow color. Apparently, the aqueous phase contains some molecules of di-β-naphthylthiocarbazone (H_mDnz), which are dissociated into Dnz^{-m} anions and mH^+. On increasing the pH of the aqueous phase, the concentration of Dnz^{-m} anions increases. The dissociation constant of di-β-naphthylthiocarbazone as an acid is expressed as follows:

$$K_{diss.} = \frac{[H^+]^m[Dnz^{-m}]_{H_2O}}{[H_mDnz_{H_2O}} \qquad (1)$$

$[Dnz^{-m}]_{H_2O}$ is the concentration of di-β-naphthylthiocarbazone anions in the aqueous phase; $[H_mDnz]_{H_2O}$ is the concentration of undissociated molecules of di-β-naphthylthiocarbazone in the aqueous phase. The value of $[H_mDnz]_{H_2O}$ is connected with the distribution coefficient, and the concentration of di-β-naphthylthiocarbazone $[H_mDnz]_{CCl_4}$ in the CCl_4 phase.

$$K_{distrib.} = \frac{[H_mDnz]_{H_2O}}{[H_mDnz]_{CCl_4}}. \qquad (2)$$

Substituting the value of $[H_mDnz]_{H_2O}$ from equation (2) in equation (1), we get

$$K_{diss.} K_{distrib.} = \frac{[H^+]^m [Dnz^{-m}]_{H_2O}}{[H_mDnz]_{CCl_4}} = K_{H_mDnz}. \tag{3}$$

Both the value of $[H_mDnz]_{CCl_4}$ and of $[Dnz^{-m}]_{H_2O}$ are readily determined photocolorimetrically. It is therefore possible to calculate the value of K_{H_mDnz}. The conclusions given here as well as the experimental method and calculations are similar to those published in the literature for dithizone [4].

The results obtained are given in Table 1.

TABLE 1

pH of aqueous phase	Di-β-naphthylthiocarbazone found			K_{HDnz}	K_{H_2Dnz}
	In CCl_4 phase	In H_2O phase	Total		
	In millimoles				
10.9	$8.6 \cdot 10^{-5}$	$0.32 \cdot 10^{-5}$	$8.92 \cdot 10^{-5}$	$2.37 \cdot 10^{-13}$	$3.0 \cdot 10^{-24}$
11.0	$7.63 \cdot 10^{-5}$	$0.42 \cdot 10^{-5}$	$8.05 \cdot 10^{-5}$	$1.84 \cdot 10^{-13}$	$1.84 \cdot 10^{-24}$
11.4	$7.1 \cdot 10^{-5}$	$0.66 \cdot 10^{-5}$	$7.86 \cdot 10^{-5}$	$2.0 \cdot 10^{-13}$	$0.8 \cdot 10^{-24}$
11.9	$5.2 \cdot 10^{-5}$	$2.09 \cdot 10^{-5}$	$7.29 \cdot 10^{-5}$	$2.5 \cdot 10^{-13}$	$0.31 \cdot 10^{-24}$
12.1	$5.5 \cdot 10^{-5}$	$2.7 \cdot 10^{-5}$	$8.2 \cdot 10^{-5}$	$1.97 \cdot 10^{-13}$	$0.15 \cdot 10^{-24}$

As can be seen from this table, the calculated values for K_{H_2Dnz} are in fair agreement between themselves while the values for K_{H_2Dnz} are not.* Consequently, it may be reckoned that di-β-naphthylthiocarbazone is a monobasic acid with $K_{HDnz} = 2.1 \cdot 10^{-13}$. Theoretical calculations of the distribution of di-β-naphthylthiocarbazone between the aqueous and CCl_4 layers, made from the values of K_{HDnz} and the values of K_{H_2Dnz} (Table 2), lead to the same conclusion. Comparison of the calculated and experimentally determined values shows that di-β-naphthylthiocarbazone is a monobasic acid.

TABLE 2

pH of aqueous phase	Di-β-naphthylthiocarbazone in the aqueous phase in %		
	$K_{dist.}$ found experimentally	$K_{dist.}$ calculated on basis of	
		K_{HDnz}	K_{H_2Dnz}
10.9	3.6	3.4	1.6
11.0	5.2	4.0	2.8
11.4	9.0	9.0	13.8
11.9	28.8	25.4	61.5
12.1	32.9	34.6	77.2

Absorption Curves for the Bismuth and Nickel Complexes in CCl_4

Absorption curves for the bismuth and nickel complexes in CCl_4 were taken by means of an FM photometer, using a cell with 1 cm layer thickness. Solutions of bismuth and nickel respectively were prepared in buffer solutions having pH values of 7.2 (for bismuth) and 8.0 (for nickel); these values of the pH ensured most complete extraction of the complexes into the CCl_4 phase. By shaking 10 ml of a solution of di-β-naphthylthiocarbazone ($0.9 \cdot 10^{-5}$ M) with 10 ml of a solution of a bismuth or nickel salt ($1 \cdot 10^{-4}$M), solutions of the complex in CCl_4 obtained. The colored CCl_4 layer was washed with distilled water purified with di-b-naphthylthiocarbazone, and transferred to the photometer cell.

Results of these measurements are given in Fig. 1 (Curve II – for the nickel complex, Curve III – for bismuth complex). For the nickel complex the molar extinction coefficient is 90,000 while for the bismuth complex it is 170,000. It is known that the molar extinction coefficient for nickel dithizonate is 30,000 while for bismuth cithizonate the corresponding figure is 45,000 [5]. Thus, di-β-naphthylthiocarbazone has undoubted advantages over dithizone with respect to sensitivity.

Composition of the Bismuth and Nickel Complexes

The composition of the complexes were determined as follows. Into a separating funnel was introduced differing volumes of solutions of nickel and bismuth salts respectively, and di-β-naphthylthiocarbazone of equal

---

* As in original – Publisher.

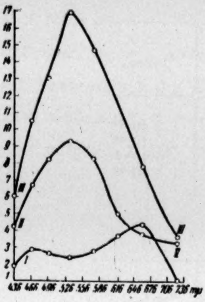


Fig. 1

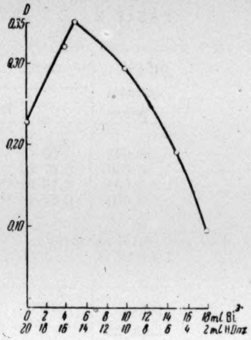


Fig. 2

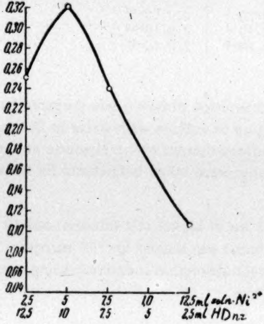


Fig. 3

molarity, the total volume being kept constant in each case. After shaking, the colored CCl_4 layer was removed into another separating funnel, washed with distilled water, and diluted with CCl_4. The volume of CCl_4 added was equal to the volume of the aqueous phase. The absorption of the diluted colored layer of CCl_4 was measured on the photocolorimeter. The ratio of the volumes at which the light absorption has its maximum value determines the composition of the complex. The results of these tests which are given in Fig. 2 (bismuth complex) and Fig. 3 (nickel complex), indicate that the composition of the bismuth complex is $BiDnz_3$, while that of the nickel complex is $NiDnz_2$.

Extraction Constants of the Bismuth and Nickel Complexes

To determine the extraction constants of the bismuth complex an exactly 0.1 N sulfuric acid solution was prepared. More diluted sulfuric acid solutions were prepared from this. The acid solutions were purified with dithizone. Experiments were carried out as follows. To 4 ml of a solution of the bismuth salt ($1 \cdot 10^{-5}$M) in a separating funnel was added 5 ml of the sulfuric acid solution of known normality, and 12 ml of the di-β-naphthylthiocarbazone solution in CCl_4. After shaking (100 seconds), allowing the layers to separate, and washing, the colored CCl_4 layer was transferred to a photocolorimeter cell, and measurements carried out using a red filter (maximum absorption at 496 - 533 mμ). The amount of complex formed was calculated by comparing with values obtained beforehand with definite amounts of complex. The extraction constant was calculated by means of the equation:

$$K_{\text{extraction}} = \frac{[Me^{3+}]\,[HDnz]^3\,[K_{HDnz}]^3}{[MeDnz_3]\,[H^+]^3},$$

where $[Me^{3+}]$ is the equilibrium concentration of the metal in the aqueous phase; [HDnz] – the equilibrium concentration of di-β-naphthylthiocarbazone in carbon tetrachloride; $[MeDnz_3]$ – equilibrium concentration of complex in CCl_4; $[H^+]$ – hydrogen ion concentration of the aqueous phase; K_{HDnz} – dissociation constant of di-β-naphthylthiocarbazone. Treatment of the experimental results (Table 3) showed that the extraction constant of the bismuth complex is given by

$$K_{BiDnz_3} = 1.5 \cdot 10^{-49}.$$

TABLE 3

$[H^+]$ in aqueous phase	$[Bi^{3+}]$	$[HDnz]$	$[BiDnz_3]$	K_{BiDnz_3}
	In millimoles			
0.005	$0.60 \cdot 10^{-5}$	$0.10 \cdot 10^{-5}$	$3.0 \cdot 10^{-6}$	$1.3 \cdot 10^{-49}$
0.016	$0.67 \cdot 10^{-5}$	$0.30 \cdot 10^{-5}$	$2.3 \cdot 10^{-6}$	$2.0 \cdot 10^{-49}$
0.030	$0.73 \cdot 10^{-5}$	$0.43 \cdot 10^{-5}$	$1.9 \cdot 10^{-6}$	$1.5 \cdot 10^{-49}$
0.050	$0.84 \cdot 10^{-5}$	$0.64 \cdot 10^{-5}$	$1.3 \cdot 10^{-6}$	$1.3 \cdot 10^{-49}$

TABLE 4

pH of aqueous phase	$[Ni^{2+}]$	$[HDnz]$	$[NiDnz_2]$	K_{NiDnz_2}
	In millimoles			
5.0	$0.81 \cdot 10^{-5}$	$0.42 \cdot 10^{-5}$	$2.9 \cdot 10^{-6}$	$2.0 \cdot 10^{-26}$
5.2	$0.78 \cdot 10^{-5}$	$0.34 \cdot 10^{-5}$	$3.3 \cdot 10^{-6}$	$2.8 \cdot 10^{-26}$
5.4	$0.73 \cdot 10^{-5}$	$0.20 \cdot 10^{-5}$	$4.0 \cdot 10^{-6}$	$2.0 \cdot 10^{-26}$

To determine the extraction constant of the nickel complex a stock solution of $NiSO_4$ was prepared by dissolving 1.8672 g of NiO in 1.6 ml of sulfuric acid (Sp.gr. 1.80) and making up to volume with water to 250 ml. From this solution a $1 \cdot 10^{-5}$M solution of the nickel salt was prepared. Buffer solutions of 0.2 N acetic acid and 0.2 N sodium acetate were purified with dithizone. Optical density readings were taken beforehand for known amounts of the nickel complex.

In a separating funnel were placed 10 ml of buffer solution, 5 ml of nickel salt solution, and 10 ml of a solution of di-β-naphthylthiocarbazone in CCl_4 ($1 \cdot 10^{-5}$M). The funnel was shaken for 100 seconds. The colored layer of CCl_4 was transferred to the photocolorimeter cell and its light absorption measured, using a red filter. The value found for the extraction constant of the nickel complex was

$$K_{NiDnz_2} = 2.3 \cdot 10^{-26}.$$

Experimental results are given in Table 4. Calculations were made on the basis of the following equation

$$K_{extraction} = \frac{[Me^{3+}]\,[HDuz]^3\,[K_{HDnz}]^3}{[MeDnz_3]\,[H^+]^3}.$$

SUMMARY

1. A solution of di-β-naphthylthiocarbazone in CCl_4 has two light absorption maxima at 665 and 450mμ. The molar extinction coefficient is equal to 40,000.

2. The value found for the dissociation constant $K_{HDnz} = 2.1 \cdot 10^{-13}$, shows that the bond with hydrogen in the NH group of the reagent is more stable in di-β-naphthylthiocarbazone than in dithizone (here $K_{HDnz} = 2 \cdot 10^{-9}$).

3. Light absorption by solutions of the complexes of nickel and bismuth respectively in the visible part of the spectrum has been studied. The positions of the maxima are favorable for colorimetric measurements. The molar extinction coefficient for the bismuth complex is 170,000 and 90,000 for the nickel complex.

4. The composition of the bismuth and nickel complexes of di-β-naphthylthiocarbazone, respectively, corresponds to the formulas $BiDnz_3$ and $NiDnz_2$.

5. The extraction constants of the bismuth and nickel complexes are $K_{BiDnz_3} = 1.5 \cdot 10^{-49}$ and $K_{NiDnz_2} = 2.3 \cdot 10^{-26}$.

LITERATURE CITED

[1] A. K. Babko and A. T. Pilipenko, Colorimetric Analysis (Moscow, State Chem. Press, 1951).

[2] H. Fischer, Angew. Chemie 50, 919 (1937).

[3] I. B. Suprunovich, J. Org. Chem. 8, 839 (1938).

[4] A. K. Babko and A. T. Pilipenko, J. Anal. Chem. 1, 275 (1946).

[5] A. T. Pilipenko, J. Anal. Chem. 8, 286 (1953) (T.p. 317).*

Received March 10, 1956

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

COLOR REACTIONS FOR DETECTING COBALT AND BISMUTH

R. B. Golubtsova

The A. A. Baikov Institute of Metallurgy, Academy of Sciences, USSR

Most of the reactions described in the literature for the qualitative detection of cobalt and bismuth are based on the use of organic reagents. During recent years, the following reagents have been suggested for detecting cobalt: dimethylglyoxime [1], nicotine in the presence of ammonium thiocyanate [2], and thiourea [3], while for detecting bismuth thiourea [4], morpholine in the presence of potassium iodide [5], and a number of dry reactions based on trituration methods [6,7], have been suggested.

In the course of the work described in the present article, conditions for the application of β-naphthoxyquinoline (in the presence of ammonium thiocyanate) as a reagent for micro- and macrochemical detection of cobalt and bismuth have been studied, and techniques have been worked out for detecting these elements in certain minerals and metals (by a non-sampling method).

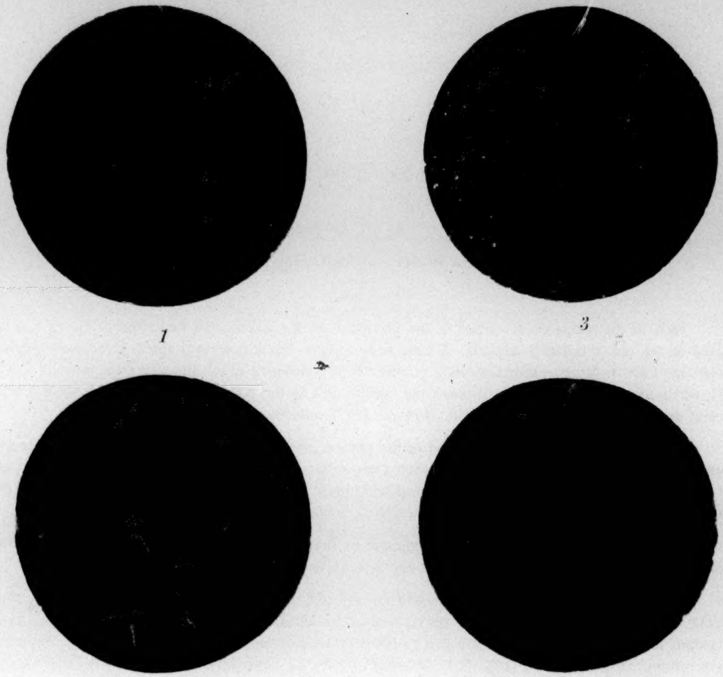
β-Naphthoxyquinoline which was suggested by Berg and Wurm [8,9], for determining cadmium as the complex $(C_{13}H_9N)_2 H_2CdI_4$, has found wide use in analytical practice.

A. Pass and A. M. Ward have suggested the use of β-naphthoxyquinoline for determining zinc [10], Hecht and Reissner have used α-naphthoxyquinoline for determining bismuth as $(C_{13}H_9N)HBiI_4$ [11]. B. A. Platunov and N. A. Kirilova were the first to use β-naphthoxyquinoline as a substitute for cinchonine for determining tungsten in ores [12]. R. B. Golubtsova [13-16], have developed a method for determining tungsten in complex and multi-component alloys, based on the use of β-naphthoxyquinoline. R. B. Golubtsova and F. M. Shemyakin were the first to use β-naphthoxyquinoline for determining molybdenum in steels and ferromolybdenum [17]. These same authors proposed the use of β-naphthoxyquinoline for specific determination of the perchlorate ion [18]. Feinberg [19], pointed out the possibility of determining small amounts of cadmium in the presence of large amounts of zinc by means of β-naphthoxyquinoline.

As Berg and Wurm [9], have pointed out, β-naphthoxyquinoline in the presence of bromide, iodide, chloride, and thiocyanate ions forms sparingly soluble salts with the following cations: Hg, Bi, Cu, Cd, Ni, Co, Zn, U, Fe^{III}. They developed a method for quantiative determination of cadmium. The mechanism of this reaction is the same as that for other organic bases, e.g., acridine [20,21].

We have established the conditions for detecting cobalt and bismuth by means of β-naphthoxyquinoline (in the presence of ammonium thiocyanate). In order to find out about the specificity of β-naphthoxyquinoline (in the presence of ammonium thiocyanate) as a reagent for identifying cobalt and bismuth, qualitative tests were carried out with various cations. On adding a 2% solution of β-naphthoxyquinoline (2 g reagent was dissolved in 100 ml water acidified with a few drops of sulfuric acid sp.gr. 1.84) in the presence of a 10% ammonium thiocyanate solution, Cd^{II}, Zn^{II}, Pb^{II}, W^{VI} gave cream-colored amorphous precipitates, while Co^{II}, Bi^{III}, Fe^{III}, and Cu^{II} gave characteristic brightly colored precipitates (See the colored photographs).

Addition of just β-naphthoxyquinoline on its own or of ammonium thiocyanate, also on its own, to solutions of the salts indicated does not lead to formation of precipitates. The latter are only formed when β-naphthoxyquinoline and ammonium thiocyanate are present simultaneously. The precipitates obtained in the case of cobalt and bismuth, after centrifuging, were carefully dried in a drying oven, first at 40°, and then at 70° to constant weight (the precipitates melt at higher temperatures). Freshly filtered precipitates dissolve readily in hot water, and also in alcohol and ether. Precipitates dried at 70° do not dissolve in hot



1 3 2 4

Reactions products of β-naphthoxyquinoline, in the presence of ammonium thiocyanate, with the salts of (1) cobalt; (2) bismuth; (3) iron; and (4) copper.

water, alcohol, or benzene, but partly dissolve in ether and acetone in the cold; they readily dissolve in aqua regia and in concentrated mineral acids on heating.

Determination of the composition of precipitates of bismuth and cobalt prepared in the same way, gave reproducible results.

Composition of the Bismuth Precipitate in %

C	H	N	Bi
49.02	2.85	11.27	18.81
48.71	2.80	11.17	18.72
48.80	2.72	11.87	19.10

Calculated for $(C_{13}H_9N)_3 \cdot H_3[Bi(SCN)_6]$ in %: C 49.20; H 2.83; N 11.48; Bi 19.05.

Composition of the Cobalt Precipitate in %

C	H	N	Co
56.02	3.25	12.80	8.88
56.12	3.33	12.69	8.76
56.09	3.40	12.73	8.76

Calculated for $(C_{13}H_9N)_2 \cdot H_2[Co(SCN)_4]$ in %: C 55.25; H 3.10; N 12.88; Co 9.03.

Thus, the composition of the precipitate should correspond to the following formula: $(C_{13}H_9N)_3 \cdot H_3[Bi(SCN)_6]$ (Molecular weight 1097).

Microcrystalloscopic detection of cobalt and bismuth. In succession, the following are placed on the object glass of a microscope; a drop of test solution, a drop of a 10% solution of ammonium thicyanate, and 1-2 drops of a 2% solution of β-naphthoxyquinoline.

After mixing the solutions, in order to form distinct crystals, the object glass is dried in a desiccator, and the characteristic colored crystals examined under the microscope. (Figs. 1 and 2).

Qualitative (microchemical) detection of cobalt and bismuth. To a drop of a neutral or weakly acid test solution in a white porcelain basin (d = 4.5 cm) is added one drop of a 10% solution of ammonium thiocyanate and one drop of a 2% solution of β-naphthoxyquinoline. In the presence of cobalt a turquoise blue precipitate is formed. At low cobalt concentrations the precipitate has a green color. Limit of identification 0.55γ Co. Limiting dilution 1:182,000. In the presence of bismuth a yellow-orange precipitate is formed. Limit of identification 4γ Bi. Limiting dilution 1:100,000.

For detecing small amounts, it is best to carry out the reaction in small volumes. For detecting cobalt and bismuth in dilute solutions, the test solution is evaporated and carefully dried (not overdried). 1-2 drops of water are then added, followed by a drop of 10% ammonium thiocyanate solution, and 1 drop of a 2% solution of β-naphthoxyquinoline.

Detection of other elements. Under the conditions described colored reactions are obtained with ferric and copper salts respectively. Limit of identification 1γ Fe. Limiting dilution 1:100,000. The precipiate has a rose color. At high concentrations the precipitate has a cherry-red color. The limit of identification for copper is 1γ. Limiting dilution 1:20,000. The precipitate is yellow. At high copper concentrations it has a chocolate brown color.

TABLE 1

Microchemical Detection of Cobalt in the Presence of Other Metals

Minimum cobalt concentration 1:180,000

Salt solutions	Other element	Limiting ratio Co: Me (in γ)
$NiCl_2 \cdot 6H_2O$.	Ni^{II}	2 : 500
$Pb(NO_3)_2$ . .	Pb^{II}	2 : 500
$ZnSO_4 \cdot 7H_2O$.	Zn^{II}	2 : 200
$K_2Cr_2O_7$ . . .	Cr^{VI}	2 : 40
$FeCl_3 \cdot 6H_2O$.	Fe^{III}	5,5 : 100
$Bi(NO_3)_3 \cdot 5H_2O$	Bi^{III}	5.5 : 75
$CuSO_4 \cdot 5H_2O$.	Cu^{II}	5.5 : 5

TABLE 2

Microchemical Detection of Bismuth in the Presence of Other Metals

Salt solutuions	Other ele-ment	Limiting ratio Bi : Me (in γ)	Minimum Bismuth concentration
$Pb(NO_3)_2$ . . .	Pb^{II}	5 : 1500	1 : 100 000
$ZnSO_4 \cdot 7H_2O$ . .	Zn^{II}	5 : 150	1 : 100 000
$Cd(NO_3)_2 \cdot 4H_2O$	Cd^{II}	5 : 150	1 : 10 000
$NiCl_2 \cdot 6H_2O$ . .	Ni^{II}	5 : 100	1 : 100 000
$K_2Cr_2O_7$	Cr^{VI}	5 : 25	1 : 100 000
$CuSO_4 \cdot 5H_2O$ . .	Cu^{II}	10 : 5	1 : 10 000
$FeCl_3 \cdot 6H_2O$ . .	Fe^{III}	4 : 1	1 : 10 000

The reactions for detecting cobalt, bismuth, iron and copper with the help of β-naphthoxyquinoline are suitable for both macro- and microchemical detection.

Microchemical detection of cobalt and bismuth in the presence of iron. In such cases, to the test solution in the porcelain basin after addition of 1-2 drops of 10% ammonium thiocyanate solution, is added one or two grains of stannous chloride, and the basin shaken until the salt has dissolved completely. Disappearance of the brown color indicates reduction of iron. If the color does not disappear, then another crystal of stannous chloride should be added. Finally, 1-2 drops of the β-naphthoxyquinoline solution is added and the appearance of a colored precipitate observed.

Spot Test for Cobalt. A drop of solution (0.01 ml) containing 1γ Co is placed on a filter paper; this is allowed to dry slightly, a drop of 10% ammonium thiocyanate solution is then placed on the first drop, followed by a drop of 2% β-naphthoxyquinoline solution. If iron should be present in the test solution, it is reduced with stannous chloride (0.01 ml) before addition of the β-naphthoxyquinoline. Limit of identification 1γ Co. Limiting dilution 1 : 10,000.

Detection of cobalt or bismuth in the presence of other metals. The reactions are carried out in this case as described above. The colored precipitate formed is compared with that from a blank. When iron is present, the technique described above is adopted.

Results on the detection of cobalt and bismuth in the presence of other metals in standard solutions are given in Tables 1 and 2.

Detection of Cobalt in the Mineral Cobalite CoArS (8-16% Fe)

A small lump of mineral contained in a small porcelain basin is covered with a mixture of acids consisting of 1 drop H_2SO_4 sp. gr. 1.84, 1 drop of HNO_3 sp. gr. 1.40, and 1.40 drop HCl (1 : 1). The basin is carefully heated for 1-2 minutes on an electric hot plate (on asbestos). By use of a glass rod, the undissolved piece of mineral is then withdrawn from the solution, washed with water, and the wash water added to the contents of the porcelain basin. The contents of the basin are evaporated almost to dryness, and then 1-2 drops of water added, followed by 1-2 drops of 10% ammonium thiocyanate, 1-2 grains of stannous chloride (to reduce the iron), and 1-2 drops of a 2% β-naphthoxyquinoline solution.

A blue precipitate of the cobalt complex is formed.

Detection of bismuth and bismutite: Bi_2S_3 (81.2% Bi) and in Cosalite: 2 PbS · Bi_2S_3 (29.46% Bi), 50.84% Pb, 19.7% S.

A lump of mineral is dissolved in 1-2 drops of HNO_3 sp. gr. 1.40 in a porcelain basin, or 1-2 drops of HNO_3 sp. gr. 1.40 placed on the surface of the mineral; after 2 minutes the liquid is transferred or poured into the porcelain basin, and the solution evaporated. 1-2 drops of a 10% ammonium thiocyanate solution is added, followed by 1-2 drops of 2% β-naphthoxyquinoline solution. A yellow-orange precipitate of the bismuth complex is formed.

Detection of Cobalt and Bismuth in Metals by the Nonsampling Method

The reactions described for detecting cobalt and bismuth were used for distinguishing metallic cobalt and bismuth from other metals. For this purpose a drop of HNO_3 sp. gr. 1.40 was placed on a bit of the metal surface cleaned beforehand with emery paper, and allowed to remain in contact with the metal for a few seconds. The acid was then transferred or washed from the metal surface to a porcelain basin, and ammonium thiocyanate and β-naphthoxyquinoline solutions added. A colored precipitate formed immediately.

SUMMARY

The behavior of β-naphthoxyquinoline with the salts of various metals in the presence of ammonium thiocyanate has been studied. Colored reactions for cobalt and bismuth, based on formation of characteristic brightly colored precipitates, allow one to detect 0.55 γ Co at a limiting dilution of 1: 182000 and 4γ Bi at a limiting dilution of 1 : 100,000.

These reactions can be used for macro- and microchemical (including spot and microcrystalloscopic) detection of cobalt and bismuth in the presence of other metals and in certain minerals and alloys.

LITERATURE CITED

[1] V. N. Podchainova and V. I. Butorin, Trans. Commission on Analytical Chemistry, Vol. III, 261 (1952).

[2] S. E. Burkat, E. N. Skrynnik, and S. S. Yaroslavskaya, J. Anal. Chem. 6, 325 (1951).

[3] G. S. Goldberg, J. Anal. Chem. 9, 56 (1954) (T. p. 63).*

[4] K. B. Yatsimirsky and A. A. Astasheva, J. Anal. Chem. 7, No. 1 (1952).

[5] M. V. Rodina, J. Anal. Chem. 7, 312 (1952) (T. p. 349).*

---

* T. p. = C. B. Translation pagination.

[6] P. M. Isakov, J. Anal. Chem. 6, 281 (1951).

[7] E. P. Ozhigov, J. Anal. Chem. 13, 175 (1953)(T.p. 193).*

[8] R. I. Berg, J. Prakt. Chem. 2, 115, 178 (1927).

[9] R. I. Berg and O. Wurm, Ber. 60, 1664 (1927).

[10] A. Pass, A. M. D. S. Ward, Analyst 58, 667 (1933).

[11] F. Hecht, and R. Reissner, Z. anal. Chem. 103, 88 (1935).

[12] B. A. Platunov and N. A. Kirillova, Sci. Records Leningrad State University, 1940, No. 5.

[13] R. B Golubtsova, J. Anal. Chem. 3, 2 (1948).

[14] R. B. Golubtsova, J. Anal. Chem. 6, 357 (1951).

[15] R. B. Golubtsova, Factory Lab. 4, 412 (1952).

[16] R. B. Golubtsova, J. Aviation Ind. 3, 36 (1952).

[17] R. B. Golubtsova and F. M. Shemyakin, J. Anal. Chem. 4, 232 (1949).

[18] F. M. Shemyakin and R. B. Golubtsova, Factory Lab. 9, 1062 (1951).

[19] S. Yu. Fainberg, Analysis of Non-Ferrous Metal Ores, (Metallurgical Press, 1953), p. 536.

[20] A. Martini, Mikrochemie 8, 144 (1930).

[21] A. Langer, Mikrochemie ver. Mikrochim. Acta 25, 71 (1938).

Received August 28, 1955

---

*T.p. = C. B. Translation pagination.

BLANK

PAGE

PHOTOMETRIC DETERMINATION OF GERMANIUM AS GERMANOVANADOMOLYBDIC ACID

Z. F. Shakhova and R. K. Motorkina

The M. V. Lomonosov Moscow State University

Germanovanadomolybdic acid was first prepared by B. N. Ivanov-Emin [1]. He also suggested that germanium could be determined colorimetrically in the form of this compound, since it has a sufficiently intense color.

Absorption curves of aqueous solutions of the heteropoly acids of germanium (Fig. 1) show that the introduction of vanadium into the heteropoly anions of germanomolybdic and germanotungstic acids significantly enhances the light absorption of the latter in the visible spectrum, and consequently increases the sensitivity of the reaction. Germanovanadomolybdic acid exhibits a considerably higher light absorption in the region 320-600 mμ, than germanomolybdic acid. The orange color of germanovanadomolybdic acid is more suitable for visual colorimetric estimation than the lemon yellow color of germanomolybdic acid in the method described already [2].

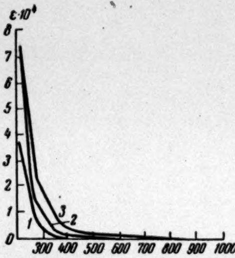


Fig. 1. Absorption curves for aqueous solutions of ammonium paramolybdate (1), germanomolybdic acid (2), and germanovanadomolybdic acid (3) in terms of molar coefficients of light absorption.

Accordingly, we decided to investigate the conditions for photometric determination of germanium as germanovanadomolybdic acid.

Since a mixture of ammonium molybdate and vanadate, when excess of the latter is present, possesses an intense color, then attempts at getting germanovanadomolybdic acid in solution containing small amounts of germanium and excess ammonium vanadate and molybdate did not give the desired results. During work with ammonium salts, the color of a "blank" was completely non-reproducible as a consequence of the comparatively low solubility of ammonium vanadate. The vanadomolybdic compound which has a bright orange color, can be extracted by all organic solvents used for extraction of heteropoly acids, if the reaction mixture is kept beforehand at an acid concentration of 0.2-0.5 N (which is essential for complete formation of the germanic complex). The color of a "blank" is also non-reproducible in this case also, as consequence of high vanadate and molybdate concentration in solution. On the basis of our numerous experiments, it is possible to conclude that germanovanadomolybdic acid can be used for colorimetric determination of germanium, only under conditions where excess vanadate has been removed from solution after formation of the germano complex (as experiments on its synthesis showed, the presence of excess vanadate is essential). On the other hand, as spectrophotometric studies of heteropoly acids showed, formation of the heteropoly anion containing germanium is preceded by formation of complex isopoly anions structurally similar to the heteropoly anion, which appear to be structural material for formation of the heteropoly anions. It might be postulated that if the vanadomolybdic hetero or aqua-poly anion is formed beforehand in solution, then it should react readily with germanium even in the absence of a large excess of vanadate.

On the basis of the considerations outlined above, we developed two variants of the photometric method of determining germanium in the form of germanovanadomolybdic acid. One of these variants repeats the conditions for its microsynthesis, while the second is based on the use of a vanadomolybdic complex prepared beforehand at a known hydrogen ion concentration.

The first variant consists of the following: to 0.01 – 1 mg of GeO_2 contained in a 15 – 20 ml beaker is added 0.5 ml of a 5% solution of ammonium molybdate, and 0.05 – 0.12 ml of 2 N sulfuric acid (the volume of sulfuric acid taken is such that its total concentration in solution is 0.2 N). The solutions are left for 10 minutes for full development of the yellow color. 5 ml of a 2% solution of $NaVO_3$, preliminarily neutralized with 2N sulfuric acid to Methyl Orange paper, is then added, followed by 0.8 ml of 2N sulfuric acid; the solution is brought to the boil and boiled for 1-2 minutes. When this is done a bulky amorphous dark brown precipitate of hydrated vanadium oxide separates out. Solution and precipitate are heated for 30 minutes on a boiling water bath: the precipitate is filtered off, and washed 3-4 times with a 10% solution of ammonium chloride, since on washing with water or with a less concentrated NH_4Cl solution the precipitate is peptized.

Filtrate plus wash water are combined in a colorimeter tube, diluted with water to 40 ml and the optical density of the final solution measured on a spectrophotometer at 400 mμ using a slit width of 0.069 mm in cells with a layer thickness of 10 mm. The wavelength indicated was chosen because at lower wavelengths, absorption of the blank is too high, while at higher wavelengths, the sensitivity drops off.

Any colorimeter which operates at this wavelength can be used for measurements.

TABLE 1
Light Absorption of the Blank Solution with Respect to Wavelength

λ mμ	D
320	0.990
330	0.810
340	0.625
350	0.447
360	0.303
370	0.204
380	0.145
390	0.111
400	0.087

TABLE 2
Determination of Germanium as Germanovanadomolybdic Acid by Means of the First Variant

GeO_2 taken in mg	D	GeO_2 found in mg	Error in mg
0.01	0.089	0.01	0.00
0.03	0.104	0.03	0.00
0.05	0.121	0.051	+0.001
0.07	0.135	0.07	0.00
0.45	0.205	0.45	0.00
0.55	0.245	0.55	0.00
0.75	0.330	0.76	+0.01
0.95	0.425	0.96	+0.01

Changes in the light absorption of the "blank" with wavelength is shown in Table 1.

The color of the "blank" is fairly reproducible under these conditions.

From the calibration curve (Fig. 2) the amount of germanium is found (Table 2). The optical density of all solutions were measured with respect to the "blank".

The low results obtained in a number of cases when large amounts of GeO_2 were present are explained by the fact that the precipitates formed strongly adsorb the heteropoly acid. For amounts of $GeO_2 > 0.5$ mg, the number of washings must be increased to 6-7. The calibration curve for 0.01 – 0.1 mg of GeO_2 is given in Fig. 3, while results for determination of GeO_2 are given in Table 2. For comparison, on Fig. 2 is shown a calibration curve for the same amounts of germanomolybdic acid. The color of the germanovanadomolybdic acid solutions obtained, is more intense than that developed from the same amounts of GeO_2, but using formation of germanomolybdic acid instead.

The high absorption in the visible region makes the reaction somewhat more sensitive during work on ordinary photometers, while the red shade of the solutions is readily applied for visual colorimetric determinations; this is an important consideration, e.g., when determining germanium under field conditions.

Both sodium and ammonium salts may be used for these determinations.

The other variant of the photometric determination of germanium as germanovanadomolybdic acid is more

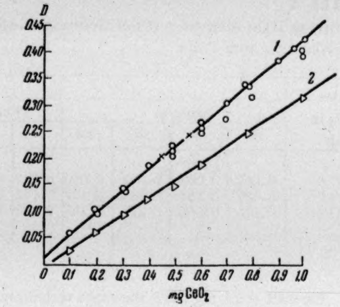


Fig. 2. Calibration curves for determination of germanium as germanovanadomolybdic acid (1) by means of the first variant, and as germanomolybdic acid (2).

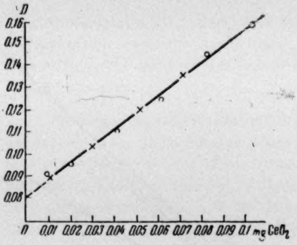


Fig. 3. Calibration curve for determining small amounts of germanium (0.01 – 0.1 mg) as germanovanadomolybdic acid by means of the first variant.

convenient; in this case, the solution of germanium dioxide is mixed with a known amount of a preliminarily prepared solution containing sodium vanadate, sodium molybdate, and hydrochloric acid.

Sodium salts should be used for preparing the reagent, since, when ammonium salts are used, a yellow precipitate forms in the reagent solution after a few hours; and moreover, the reagent solution itself is quite brightly colored in this case.

The stability of germanovanadomolybdic acid in relation to hydrogen ion concentration was studied beforehand. For preparation of the reagent 40 g of normal sodium molybdate was dissolved in 120 ml water (solution I), and independently 6 g of sodium metavanadate was dissolved in 80 ml water (solution II); the solutions were filtered and then 30 ml of solution I mixed with 20 ml solution II; various amounts of concentrated hydrochloric acid were added, and the volumes finally made up to 100 ml. 5 ml of the reagent thus obtained was used for each determination. For carrying out the colorimetric reaction, 5 ml of reagent solution was added to different amounts of GeO_2, the volume made up to 40 ml and optical density measured with respect to a blank prepared by diluting 5 ml of reagent to 40 ml; measurements were made at 400 mμ in cells with a layer thickness of 10 mm, and a slit width of 0.069 mm. A constant color was attained after 20-25 minutes which corresponded strictly to GeO_2 concentration.

By carrying out colorimetric measurements with a reagent containing various amounts of hydrochloric acid, we established the relation between the color intensity of the complex and hydrogen ion concentration. It was found that germanovanadomolybdic acid is most stable at concentrations of 0.20 – 0.28 N hydrochloric acid; the region in which it was established earlier that germanomolybdic acid was stable (0.20 – 0.50) [2]. The color of the germanovanadomolybdic complex is stable over a very wide hydrogen ion concentration when hydrochloric acid is used. Nevertheless, when acid concentration is increased beyond the optimum, decomposition of the complex is slowest when sulfuric acid is used. Accordingly, the colorimetric reaction should be carried out in the presence of hydrochloric acid, while sulfuric acid should be used for extraction.

Calibration curves for determination of germanium as germanovanadomolybdic acid when different concentrations of hydrochloric acid are used, are shown in Fig. 4. On the same figure, for comparison, is given the curve for germanomolybdic acid which was obtained under the same conditions, but without addition of sodium vanadate. It is obvious that the optical density of solutions of germanovanadomolybdic acid is considerably higher than that of germanomolybdic acid solutions, for the same amounts of germanium. The method is extremely simple and allows determinations to be carried out in the visible. The colors are also suitable for visual colorimetry.

The color of the solutions is very stable even at the highest permissible acidity (0.28 N) (Table 3).

The reagent for colorimetric determinations should be prepared in small amounts every 1-2 days, since after 2-3 days a yellow precipitate separates out. The reagent is stable in more acid solutions.

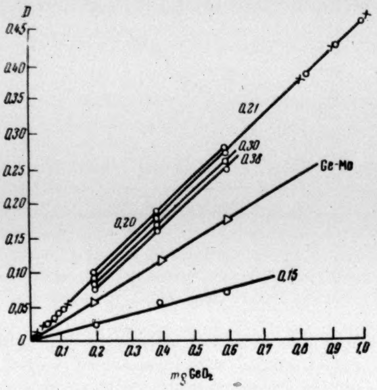


Fig. 4. Calibration curves for determination of germanium as germanovanadomolybdic acid, using the second variant, for different hydrogen ion concentrations.

TABLE 3

Changes in Light Absorption (D) of Germanovanadomolybdic Acid with Time

Amount of GeO_2 in mg	D					
	Minutes				Hours	
	10	20	60	120	24	36
0.2	0.096	0.093	0.093	0.090	0.097	0.093
0.4	0.189	0.184	0.182	0.177	0.177	0.173
0.6	0.275	0.265	0.262	0.255	0.258	0.255

For 0.01 – 0.1 mg GeO_2 the same technique is used, but a stable color is formed more slowly (25-30 minutes). During determination of germanium by the second method, the results given in Table 4 were obtained.

Replacement of hydrochloric acid by sulfuric or nitric acid during preparation of the reagent does not have any significant effect on experimental results, but reagent solutions are less stable; accordingly hydrochloric acid is recommended for the work. Heating to 90° before carrying out colorimetric measurements has no effect on the results.

TABLE 4

Determination of Germanium as Germanovanadomolybdic Acid by the Second Variant

GeO_2 taken in mg	D	GeO_2 found in mg	Error in mg	GeO_2 taken in mg	D	GeO_2 found in mg	Error in mg
0.01	0.005	0.01	0.0	0.50	0.220	0.49	—0.01
0.01	0.007	0.011	+0.001	0.70	0.312	0.70	0.00
0.01	0.005	0.01	0.0	0.70	0.315	0.705	+0.005
0.02	0.01	0.02	0.0	0.80	0.351	0.805	+0.005
0.05	0.025	0.06	+0.01	0.90	0.405	0.90	0.00
0.07	0.030	0.07	0.00	1.00	0.445	0.995	—0.005
0.10	0.045	0.10	0.00	1.00	0.440	0.99	—0.01

Since the minimum amount of germanium dioxide which can be determined when the recommended technique is used amounts to 0.01 mg in 40 ml, while the sensitivity of the method increases on extraction, the possibility of extracting germanovanadomolybdic acid with isoamyl alcohol was studied. To 0.5 ml of the original solution of synthesized germanovanadomolybdic acid was added water, various amounts of 12 N sulfuric acid, and 6 ml of isoamyl alcohol in each case, the solutions made up to 40 ml and the whole shaken for 4 minutes. The isoamyl alcohol layer was separated in a separating funnel, filtered, and then its optical density measured in an SF-4 spectrophotometer at 400 mμ, using a slit width of 0.1 mm, and cells with layer thickness of 10 mm. A blank solution was prepared in the same way but leaving out the heteropoly acid.

Under identical conditions, 5 ml of the reagent used for colorimetric determinations was extracted, and the optical density of the solutions obtained measured with respect to the same "blank". Results of measurements are given in Fig. 5.

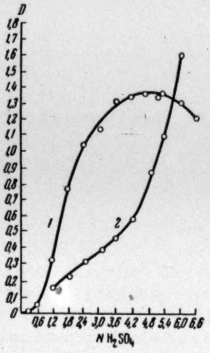


Fig. 5. Relation between color intensity of solutions of germanovanadomolybdic acid (Curve 1), and reagent (Curve 2) in isoamyl alcohol respectively, and H_2SO_4 concentration.

On Replacing the sulfuric acid used in the extraction of the reagent by hydrochloric and nitric acids respectively, the values of the optical density of the "blank" increase.

From the results thus obtained it is clear that extraction, in the given instance, does not increase reaction sensitivity, since excess reagent is strongly extracted. It follows from Fig. 5, that extraction of germanovanadomolybdic acid should be carried out from 3.6 – 5.4 N sulfuric acid. The color of excess reagent is so strong under these conditions, that measurements at 400 mμ are impossible, while at longer wavelengths, reaction sensitivity drops off rapidly.

The agreement between results obtained when determinations are carried out by either of the two methods, shows that in both cases the same compound is formed – germanovanadomolybdic acid.

SUMMARY

1. The hydrogen ion concentration range within which germanovanadomolybdic acid is stable in aqueous solutions has been studied spectrophotometrically.

2. Two variants of a photometric method of determining germanium as germanovanadomolybdic acid have been developed. The method has several advantages over the method based on the use of germanomolybdic acid.

3. It has been shown that it is not expedient to extract with organic solvents during determination of germanium as germanovanadomolybdic acid.

LITERATURE CITED

[1] B. N. Ivanov-Emin, J. Org. Chem. 19, 9, 826 (1940).

[2] Z. F. Shakhova and R. K. Motorkina, Collection: Analytical Methods for Rare Metals and Non-Ferrous Metals (Moscow State University Press, 1956), p. 47.

Received July 13, 1955

BLANK
PAGE

POLAROGRAPHIC DETERMINATION OF PALLADIUM ON SOLID ELECTRODES

M. B. Bardin and Yu. S. Lyalikov

Kishinev State University

The polarographic behavior of palladium has been studied to a comparatively small extent. Herasymenko and Slendyk [1], who discovered the catalytic liberation of hydrogen on a dropping electrode in the presence of traces of platinum, note that this effect is insignificant in the case of palladium. Willis [2], studied the polarographic behavior of palladium in solutions of potassium cyanide, ammonia, pyridine, and ethylenediamine. The wave of the cyanide complex can be used for analytical purposes. Nevertheless, Rius and Molera [3], point out that the cyanide complex of divalent palladium does not give a wave. Tomicek and coworkers [4], found that using various amines as supporting electrolytes, (diethylamine, ethylenediamine, diethylenediamine, etc.) palladium complexes give clear-cut waves which are suitable for analytical purposes.

The comparatively small amount of work carried out on the polarography of the platinum metals, including palladium, can probably be attributed to the difficulties which arise during attempts to take polarograms on a dropping mercury electrode. These difficulties are connected with the position of the platinum metals in the E. M. F. series; as a result of displacement of mercury from solutions, their determination polarographically becomes impossible.

Attempts to overcome these difficulties have been concentrated hitherto on looking for complexing agents which would give compounds of the platinum metals which are stable with respect to metallic mercury. This approach however has not always led to positive results. Quite often the stable complexes are not reduced on the dropping electrode. In other cases, polarographic determination of the platinum metals becomes impossible on account of catalytic evolution of hydrogen. There is, however, one other approach for overcoming these difficulties which has not hitherto been tried by other investigators; this is replacement of the dropping mercury electrode by a solid electrode. As a supplement to our previous work [5], we have in the work described in the present article, studied the possibility of using solid electrodes for determining palladium.

Experimental and Discussion of Results

The work was carried out on the setup described previously [5]. The concentration of the standard palladium chloride solution was determined by precipitation with dimethylglyoxime, and was found to be equal to 0.0048 g Pd in 1 ml, or 0.045 M. In order to take polarograms a known volume of the standard solution was transferred to a 25 ml standard flask, the volume made up to the mark with 0.1 M sodium nitrate which served as supporting electrolyte, and then 20 ml of this solution transferred to the electrolyzer which we have described [5], and which protects the solution from the air. Oxygen was removed by bubbling nitrogen through the solution. The current was measured a minute after applying the potential.

On a solid stationary platinum electrode, in a supporting electrolyte of 0.1 N $NaNO_3$, palladium gives a clear-cut current-voltage curve with a well-defined diffusion region. The rise on the curve (reduction potential) is observed at 0.6 – 0.7 V of the applied E. M. F. (Fig. 1).

Current-voltage curves show good reproducibility. There is no need to depolarize and clean the electrode surface after each run. On Fig. 2 are shown five polarograms taken successively in the same palladium chloride solution using the same electrode. As can be seen from Fig. 2, the nature of the curves and the wave height agree amongst themselves, while with respect to definition, they are in no way inferior to classical current-voltage curves obtained on the dropping electrode for a series of ions.

The current-voltage curve for palladium obtained on increasing the applied E. M. F. practically coincides with the curve obtained on gradually decreasing the E. M. F. to zero. This same agreement is observed with respect to potentials (Fig. 3).

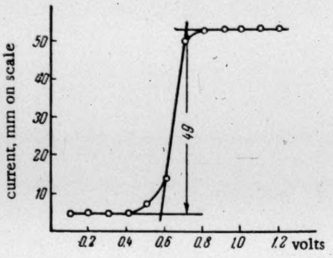


Fig. 1. Current-voltage curve for palladium (1 division of the galvanometer scale is equivalent to $1.4 \cdot 10^{-7}$, Pd concentration equal to 1.76 mg/20 ml).

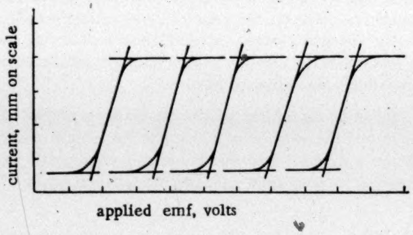


Fig. 2. Polarograms for palladium taken successively, without depolarization and purification of the electrode (1 scale division of the galvanometer is equal to $1.4 \cdot 10^{-7}$).

One of the basic criteria of the reversibility of an electrode process is the slope of the straight line $E = \log i/(i_d - i)$ [7]. Usually, for polarography with solid electrodes, the slope is considerably higher than the theoretical value of 0.059/n (at 25°), which serves as proof of the irreversibility of the process. On plotting E against logarithm $i/(i_d - i)$, in the case of reduction of palladium on a platinum and palladinized electrodes, the slope is equal to 0.080 V, i.e., considerably higher than the theoretical value of 0.030 V, thereby indicating that this process is irreversible.

This result is not unexpected, since during the taking of polarograms for palladium, the surface of the platinum microcathode is covered by a layer of metallic palladium – an electrode reaction product.

As Gokhshtein and Surkov [6] have shown that a decisive and final answer on the reversibility of a process can only be obtained by means of oscillographic polarography, it would be well worth using this means for solving the question on the reversibility of palladium reduction.

The fact that metallic palladium is deposited on the electrode surface means that the polarographic process is actually taking place on a palladinized electrode. Information has been published on studies of the properties of palladium and palladinized electrodes respectively; nevertheless there is no available data on the suitability of such electrodes for analytical purposes.

The palladinized electrode possesses a number of characteristics. When polarograms are taken at an applied potential range from 0 to 1.5 – 1.7 V (i.e., up to the point at which hydrogen is evolved), then after taking each polarogram, the polarographic wave for palladium becomes more distorted (Fig. 4). The reason for this is either the negative influence of polarization which is usual for solid electrodes, or the specific behavior of the palladinized electrode towards hydrogen evolved during electrolysis.

It is known that during the electrolytic evolution of hydrogen on palladium and palladinized electrodes the hydrogen which is evolved is adsorbed and dissolved in the metallic palladium. Consequently, it is to be expected that in our work with palladinized microelectrodes, evolution of hydrogen will be accompanied by its dissolution in the metallic palladium which is deposited as the result of an electrode reaction.

In all probability, such an electrode saturated with hydrogen will reduce palladium ions. As can be seen from Fig. 4, with increasing saturation of the electrode with hydrogen the reduction potential is displaced to more positive values, which indicates the ease with which palladium is reduced on such an electrode. When the electrode is completely saturated with hydrogen, a sharp rise on the current-voltage curve starts almost at zero applied potential.

Judging by the character of the curves, it may be postulated that dissolving of hydrogen on the palladinized microelectrode owing to the state of dispersion of the deposit of metallic palladium, will proceed quickly. As shown in Fig. 4, already after 2-3 cycles, the electrode is saturated with hydrogen, probably with formation of a β-phase.

We did not succeed in getting polarograms of a satisfactory shape on an electrode which absorbs hydrogen,

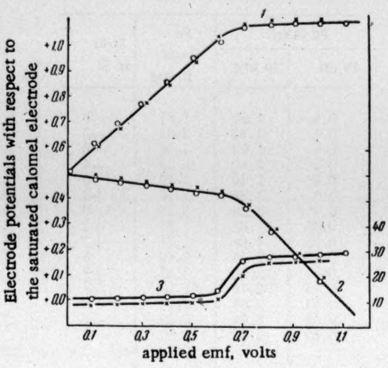


Fig. 3. Curves illustrating potential changes on the electrodes during the process of taking polarograms: O) forward ×)back 1) anode; 2) cathode; 3)current-voltage curve.

even after prolonged passage of nitrogen through the solution to be polarographed. This indicates that blowing nitrogen through the solution does not succeed in removing the dissolved hydrogen from the electrode. This is in agreement with the results of Fedorova and Frumkin [8], which they obtained during a study of the system palladium – hydrogen by the potential curves method. These authors established that at room temperature one cannot remove all the hydrogen from a palladinized electrode, even after a 15 hour passage of nitrogen through the cell. At 20.0°, they succeeded in removing approximately half of the hydrogen absorbed by the palladium by passing nitrogen through the solution.

A palladinized electrode which has absorbed hydrogen and as a consequence has become unsuitable for analytical purposes, can be readily regenerated by treating it with hot nitric acid. When this is done the palladium dissolves, while the electrode surface becomes smooth again. The electrode is then washed in distilled water. The first 2-3 polarograms for palladium obtained with such an electrode are not quite distinct, while the succeeding ones acquire their normal form and show good reproducibility. Hydrogen can also be removed by anodic polarization.

It should be noted that if one stops taking the polarogram at a potential of 1.2 – 1.3 V, before hydrogen starts to be evolved, then one can get distinct curves with good reproducibility (Fig. 2).

In weakly acid media at a potential of 0.6 – 0.7 V, a characteristic maximum (Fig. 5), develops on the current-voltage curve. As was to be expected, the maximum could not be removed by addition of surface-active materials. The maximum disappears and the polarogram resumes its normal shape on adding a small amount of hydrochloric acid (to 10 ml of the solution being polarographed, 0.2 – 0.4 ml of 0.1 M HCl is added).

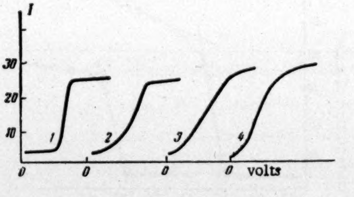


Fig. 4. Distortion of the polarographic wave after absorption of hydrogen by the electrode.

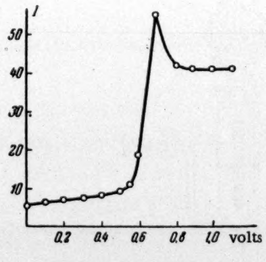


Fig. 5. Palladium polarogram with a maximum.

Within the concentration range studied there was observed a linear relation between diffusion current and palladium concentration (Fig. 6). Results of determinations of known amounts of palladium by means of the calibration curve are shown in the table. These results are in satisfactory agreement with results of gravimetric determinations of palladium. The maximum experimental error did not exceed 6%, while the average error was 3%. Since determination on a stationary electrode requires that it is necessary to wait for 1 minute to establish a constant value for the current, taking a polarogram takes not less than 12-14 minutes. Accordingly, in order to cut down the time required to make a determination, the possibility of using a rotating electrode was studied.

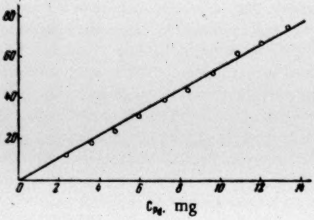


Fig. 6. Calibration curve .

TABLE

Pd taken		Pd found in mg	Error in %
in ml	in mg		
0.4	1.92	1.81	—6
0.4	1.92	1.84	—5
0.4	1.92	1.81	—6
0.5	2.40	2.33	—4
0.5	2.40	2.40	0
0.7	3.36	3.46	+3
0.7	3.36	3.36	0
0.35	1.68	1.73	+3
0.35	1.68	1.71	+2
0.45	2.16	2.16	0
0.45	2.16	2.32	+7
0.45	2.16	2.10	—3
0.55	2.64	2.74	+6
0.55	2.64	2.69	+2
0.85	3.84	3.80	—1

A suitable rotating electrode with a mercury seal for preventing contact between solution and the air was prepared, taking a model suggested by Kolthoff as a basis [9], slight modifications being introduced. The tip of the rotating iron spindle was made into a screw-on type. The platinum wire serving as cathode was fused into a glass tube. The screw-on end of the spindle was fitted into a tube and contact made by means of mercury (Fig. 7); this type of construction has a number of advantages: there is no need to cover the spindle with ceresine wax (for insulation), since the glass tube serves as a more reliable insulator; the electrode is readily removed for periodic cleaning or replacement. By changing the length of the glass tube, it is possible to regulate the depth of immersion of the electrode.

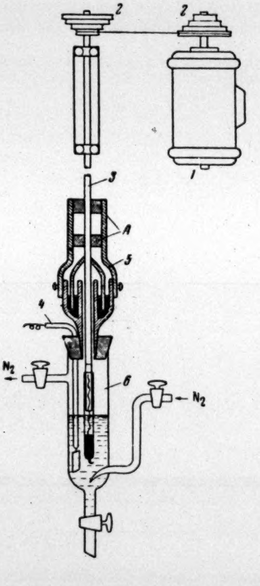


Fig. 7. Rotating electrode setup: 1) three phase motor; 2) pulley; 3) rotating spindle with cathode; 4) anode; 5) mercury seal; 6) electrometric cell; A) bronze sleeve.

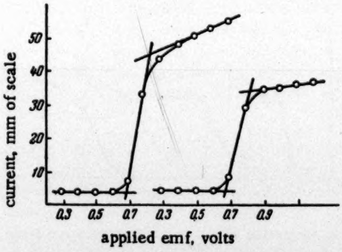


Fig. 8. Polarograms for palladium obtained on a rotating electrode; on the left – Pd concentration 0.19 mg/10 ml; on the right – Pd concentration 0.14 mg/ml (1 scale division of the galvanometer is equal to $1.4\ 10^{-6}$A).

All the results which are given were obtained with a speed of ~ 800 revolutions/minute for the rotating electrode.

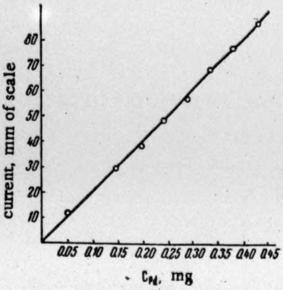


Fig. 9. Calibration curve.

Clear-cut waves were obtained on the rotating electrode as on the stationary one (Fig. 8). There is a linear relation between wave height and paladium concentration (Fig. 9).

The current is established within 15-20 seconds on a rotating electrode so that it is possible to carry out a determination fairly rapidly, and 3-4 times faster then with a stationary electrode.

In addition, the use of a rotating electrode leads to a higher sensitivity. At the lowest galvanometer sensitivity, clear-cut waves were obtained for solutions containing 0.05 mg of palladium in 10 ml of the solution being polarographed (0.0005 M), i.e., the sensitivity can exceed the normal sensitivity of a dropping mercury electrode.

In conclusion we should like to thank A. I. Shlygin for valuable advice.

SUMMARY

1. It has been shown that palladium gives a clear-cut polarographic reduction wave at 0.6 – 0.7 V on solid platinum and palladinized electrodes, respectively.

2. Under certain conditions the waves are readily reproducible without depolarization and cleaning of the electrode surface, and can be used for analytical purposes.

3. The accuracy of the polarographic determination of palladium is ± 3%, which exceeds the usual sensitivity of solid electrodes.

4. The use of a rotating electrode instead of a stationary one appreciably speeds up determination and increases the sensitivity of palladium determination.

LITERATURE CITED

[1] P. Herasymenko and J. Slendyk, Coll. Czechoslov. Chem. Commun. 5, 11, 479 (1933).

[2] J. B. Willis, J. Am. Chem. Soc. 67, 4, 547 (1945).

[3] A. Rius and M. Molera, Anales Fis. quim. (Madrid) 45, (B) 1151 (1949).

[4] O. Tomicek, J. Cihalik, J. Dolezal, V. Simon and J. Zýka, Chem. Listy 47, 3, 363 (1953).

[5] M. B. Bardin and Yu. S. Lyalikov, J. Anal. Chem. 10, 305 (1955) (T.p. 289).•

[6] Ya. P. Gokhshtein and Yu. P. Surkov, J. Anal. Chem. 9, 319 (1954) (T.p. 355).•

[7] L. I. Fedorova and A. N. Frumkin, J. Phys. Chem. 27, 2, 247 (1953).

[8] I. M. Kolthoff and J. Lingane, Polarography (Moscow – Leningrad, 1948), p. 423.

[9] I. M. Kolthoff and J. Lingane, Polarography (Moscow – Leningrad, 1948), pp. 160 and 169.

Received January 11, 1955

• T.p. = C. B. Tranlsation pagination.

BLANK
PAGE

AMPEROMETRIC TITRATION OF ZINC, COBALT, AND COPPER WITH POTASSIUM TETRATHIOCYANATOMERCURIATE

V. A. Khadeev and A. I. Mirbadaleva

The V. I. Lenin Central Asiatic State University, Tashkent

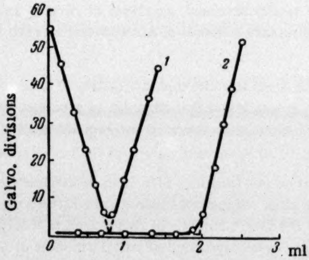
Both potassium and ammonium tetrathiocyanatomercuriate have long been used in quantitative analysis for determining zinc and some other metals by gravimetric, volumetric, colorimetric, and indirect methods.

Taking into account the capacity of tetrathiocyanatomercuriate ions to be reduced on mercury and platinum cathodes, we decided to study the possibility of using potassium tetrathiocyanatomercuriate for direct amperometric titration of zinc, cobalt, and copper cations.

The work was carried out on the visual polarograph of the Gorkovsky Institute of Chemistry. The current was measured with a mirror galvanometer type φ, with an oscillation period of 7.9 seconds, and a maximum sensitivity of $2.45 \cdot 10^{-3}$ μa on a 1 mm scale. The sensitivity usually used was 1/200. The dropping electrode had a dropping period of 3 seconds. The anode was a saturated calomel half-element connected to the solution to be titrated via a siphon filled with agar gel in potassium nitrate. Reagent was added in small aliquots from a tapless 3 ml micro-buret divided in 0.01 ml graduations. The solution was stirred with a magnetic stirrer and a stream of hydrogen. The equivalence point was found by the usual graphical method.

A standard potassium tetrathiocyanatomercuriate solution was prepared by Kolthoff's method [1] by dissolving a known weight of freshly prepared mercuric thiocyanate, which had been dried in a vacuum desiccator over sulfuric acid in a concentrated solution of potassium thiocyanate. Reagent solution of the requisite concentration was prepared by diluting the solution prepared as described above with water in a standard flask. Solutions with normalities of 0.2741 and 0.1370 were used; these contained only a very small excess of uncombined potassium thiocyanate.

All the other solutions used in the work were prepared by the normal methods from chemically pure salts. Exact standardizations of solutions of the sulfates of zinc, cobalt, and copper were carried out in replicated determinations, by means of the following methods: for zinc – gravimetrically with hydroxyquinoline and sulfate; for cobalt – the sulfate method; and for copper – electrolysis.



Titration curves for potassium tetrathiocyanatomercuriate: 1) E = 1.4 v; 2) E = 0.8 v.

The wave of tetrathiocyanatomercuriate ions in a supporting electrolyte of 0.3 M KNO_3, Na_2SO_4, and H_2SO_4, starts during the anodic polarization of the dropping electrode, and a diffusion current is obtained at an applied potential near to zero. The wave exhibits a clearly defined maximum, extending right up to a potential of 0.7 V at a concentration of $[Hg(SCN)_4]^{2-}$ of the order of 0.005 M/liter. In neutral solutions, the maximum is easily suppressed by means of Methyl Red or gelatin. In the presence of acids, the maximum is suppressed with difficulty, and then not completely. In order to avoid possible interference from polarographic maxima, all the basic experiments on titration of salts of zinc, cobalt, and copper were carried out at applied potentials exceeding 0.7 V.

Titration of Zinc

It was found that zinc sulfate solutions at concentrations greater than 0.01 mole/liter, are titrated fairly quickly and accurately. The current reaches a steady value 1-2 minutes after addition of reagent. More dilute solutions are not titrated so well because of the sharp decrease in the rate of precipitate formation. When titration is carried out at voltages exceeding 1.3 V a V-shaped titration curve is obtained. At potentials of 0.8 - 0.9 V, the titration curve obtained has a horizontal left-hand branch and an ascending right-hand one. The shapes of the titration curves are shown in the diagram.

The nitrates or sulfates of the alkali metals, as well as sulfuric or nitric acids can be used with equal success as supporting electrolytes. The concentration of any of these compounds in the solution being titrated can be brought up to 1 M without any essential effect on the nature and results of titration. Neither do the chlorides, acetates, and thiocyanates of the alkali metals, or hydrochloric acid, at concentrations less than 0.3 M, interfere with titration. Phosphoric acid has no effect on the position of the equivalence point; nevertheless, it favors a more sharp appearance of the polarographic maximum on the thiocyanatomercuriate wave, and displaces it to higher potentials. As a consequence of this, in the presence of H_3PO_4, it is difficult to get a left-hand ascending branch at potentials of 0.8 - 1.0 V, since even at very low values of excess reagent, the current becomes anomalously large and unstable with time. It was found that these anomalies can be completely removed by addition of potassium thiocyanate up to concentrations of the order of 0.2 - 0.3 M to the phosphoric acid solution being titrated.

TABLE 1

Zn taken in mg	Number of replicates	Volume of solution being titrated in ml	Zn found in mg (means of replicates)	Maximum deviation of an individual determination from the mean		Deviation between mean experimental value and amount actually taken	
				in mg	in %	in mg	in %
87.32	4	50	87.51	0.05	0.06	+0.19	0.22
69.95	4	20	70.48	0.14	0.20	+0.53	0.76
35.01	3	20	35.05	0.17	0.48	+0.04	0.11
27.65	3	20	27.58	0.14	0.50	—0.07	0.25
13.83	3	20	13.91	0.08	0.57	+0.08	0.57
6.92	3	20	6.96	0.11	1.5	+0.04	0.57
3.44	3	20	3.52	0.05	1.3	+0.08	2.32

Addition of alcohol or acetone to the solution being titrated leads to a deterioration of the titration results, as a result of an appreciable increase in solubility of the zinc thiocyanatomercuriate precipitate.

In order to establish the accuracy and reproducibility of the results obtained, titrations of varying amounts of zinc were carried out under optimum conditions (including preliminary removal of atmospheric oxygen from solution). Results of these tests are given in Table 1.

A consideration of the results given in Table 1 shows that the accuracy and reproducibility of determinations, are, in all cases except the last, completely satisfactory. Further, it was found that titration of zinc can be carried out even without preliminary removal of dissolved oxygen, without essentially lowering the reproducibility and accuracy of the results obtained.

It was found that aluminum, magnesium, and chromium ions do not interfere with zinc determinations, even in those cases where their concentrations are 2-3 times that of the zinc. Manganese ions do not interfere appreciably as long as their content in solution does not exceed 10% of that of the zinc content. In the presence of large amounts, the results for zinc are high by a few percent, presumably because of coprecipitation of small amounts of manganese thiocyanatomercuriate.

Ferrous ions interfere particularly strongly: titration results can be as much as 30% too high, when the concentration of these ions is of the same order as zinc concentration. It is only at very low iron contents in the solution to be titrated - not greater than 2% of the amount of zinc - that coprecipitation of iron barely occurs, and the results obtained are correct.

Ferric ions are coprecipitated to approximately the same extent as manganese ions. Coprecipitation can, however, be almost completely eliminated if 0.5 - 1 ml of concentrated phosphoric acid is added to 20 ml of the solution to be titrated.

Titration of Cobalt

Titration of cobalt salts was carried out at an applied potential of 0.8 V. It was found that solutions containing more than 1.5 mg of cobalt in 1 ml, are titrated fairly rapidly; it is necessary to wait 2-3 minutes after addition of reagent. The dark blue precipitate formed settles out very rapidly to the bottom. Titration of more dilute solutions is poor. As a result of the higher solubility of cobalt thiocyanatomercuriate as compared with the analogous zinc salt, titration curves for cobalt do not show such a sharp break at the equivalence point as the zinc curves. All the same, the position of the equivalence point can be established with satisfactory accuracy by projecting the linear parts of the curve to their mutual intersection. The nature of interference from other salts and acids on titration of cobalt is the same as in the case of zinc titration. The accuracy of cobalt titrations is illustrated by the results given in Table 2. Titration was carried out in a supporting electrolyte of 0.3 M Na_2SO_4 or 0.3 M H_2SO_4. The volume of solution being titrated in each case was 20 ml.

TABLE 2

Co taken in mg	Co determination		Deviation between mean values and amounts actually taken	
	Number of replicates	Co found in mg (means of replicates)	in mg	in %
153.3	2	153.6	+0.3	0.20
122.8	3	122.0	—0.8	0.65
61.46	2	61.08	—0.38	0.61
30.52	2	29.25	—1.27	4.16

Titration of Copper

Titration of copper does not give satisfactory results because of the absence of proportionality between the amount of copper taken and the volume of $K_2[Hg(SCN)_4]$ found from the titration curve. Results were always very low as compared with the theoretical values, calculated on the assumption that the composition of the precipitate corresponds to the formula $Cu[Hg(SCN)_4]$. These anomalies are connected presumably with inconstancy of the composition of the precipitate formed. In view of the relatively low solubility of cupric thiocyanate, considerable coprecipitation of this salt may occur together with copper thiocyanatomercuriate of normal composition. If this is the case then coprecipitation should increase with increasing concentration of free thiocyanate ions in the reagent. Special experiments indirectly confirmed this assumption: on adding increasing amounts of potassium thiocyanate to the working solution of reagent, there were observed larger and larger displacements of the equivalence point towards the side giving low results.

We have not come across any published work dealing with studies of the composition of precipitates of copper thiocyanatomercuriate under different conditions.

Titration of Zinc and Cobalt with a Rotating Platinum Electrode

It was found that titration of zinc and cobalt with potassium thiocyanatomercuriate can also be carried out with rotating platinum electrode. The titration method and the optimum conditions remain unchanged.

The setup described above was used for titration, the only difference being substitution of a rotating platinum electrode for the dropping electrode. The rotating electrode was a platinum wire 0.4 mm diameter, sealed in sideways to a 10 mm glass tube near its lower fused end. Best results were obtained for a short length of electrode, not exceeding 1 mm. The electrode was rotated at the rate of 800 revolutions/minute. Titration was carried out at zero potential of the rotating electrode relative to the saturated calomel electrode. The shape of the titration curves obtained is similar to that shown in the diagram. Reproducibility and accuracy of the results are the same as those obtained during titration with a dropping electrode.

SUMMARY

1. It has been shown that it is possible to carry out amperometric titrations of neutral and acid solutions of zinc and cobalt respectively with potassium tetrathiocyanatomercuriate, and optimum conditions for these titrations have been established. SO_4^{2-}, NO_3^-, $H_2PO_4^-$, Cl^-, CH_3COO^-, CNS^-, the cations of the alkali and alkaline-earth metals, as well as Al^{3+}, Cr^{3+}, and Fe^{3+}, and small amounts of Mn^{2+} do not interfere with titration. Titration can be carried out with either a dropping mercury electrode or with a rotating platinum electrode.

2. Amperometric determination of copper on the basis of formation of copper thiocyanatomercuriate is not possible because of the variable composition of the precipitate formed.

LITERATURE CITED

[1] I. M. Kolthoff and Von Dijk, Pham. Weckll, 58, 549 (1921).

Received December 23, 1954

SPECTROCHEMICAL DETERMINATION OF SMALL AMOUNTS OF VANADIUM IN SAMPLES OF COMPLEX COMPOSITION

T. M. Moroshkina and V. K. Prokofiev*

The A. A. Zhdanov Leningrad State University

Spectrographic determination of vanadium is of great interest since it permits one to determine it directly, without preliminary separation of the vanadium– a factor which cuts down the time required for analysis.

Work has been published on the spectrographic determination of more than 0.1% of vanadium in copper-bearing sands and titanomagnetites [1,2], and also in other ores [3,4].

We made it our aim to develop techniques for spectrographic determination of thousandths and ten thousandths of a percent of vanadium in samples of complex composition. The work was carried out on a Hilger autocollimating spectrograph (in the region 2600 - 4000 A). The source was an A. C. arc stabilized by an additional resistance of 80 kΩ and an Abramson attachment. The spectra were photographed at a current strength of 7 amperes and a voltage of 200 V, on "plates for scientific work Type II." Exposure time was 2 minutes. Molybdenum which had been added to the test as a solution of ammonium molybdate was used as the internal standard. The analytical pair of lines chosen were V 3183.98A and Mo 3170.35 A.

Preliminary experiments were carried out on synthetic mixtures which contained in addition to vanadium, uranium, iron, aluminum, and magnesium. Copper powder (50 mg) or a mixture of copper and silica (in the proporition of 1:4) was moistened with 0.1 ml of solution. The vanadium content of the test sample was 10^{-6} g (1γ). The absolute sensitivity of the lines chosen for vanadium was 10^{-8} g under the conditions we used.

We were interested in the possibility of determining small amounts of vanadium in ores and minerals of varying composition. It is known that the success of quantitative spectrographic determination depends, to a considerable extent, on correct choice of standards. In the case of analysis of ores and minerals of differing composition, preparation of standards which correspond fully in composition to the test samples, is very difficult. In order to overcome this difficulty we used the method of addition, i.e., standards were prepared on the basis of test samples containing C_x of vanadium [5]. Each sample was divided into four parts, to three of which was added increasing, known amounts of vanadium C: C_1, C_2 and C_3 (corresponding to $0.25 \cdot 10^{-5}$ g: $1.50 \cdot 10^{-5}$ g or $1.0 \cdot 10^{-6}$ g; $2.0 \cdot 10^{-6}$ g; $4.0 \cdot 10^{-6}$ g).

Calibration curves were constructed within the coordinates I_V / I_{Mo} and C. Since determinations of small concentrations of vanadium were performed, it was possible to ignore self-absorption and assume that b = 1. Then the analytical relation between vanadium concentration and relative intensity of the vanadium line to that of the internal standard is of the form:

$$\frac{I_V}{I_{Mo}} = a(C_x + C_g).$$

When using the method of additions, it is necessary to observe the following conditions:

1) any superposition of lines leading to distortion of the true content of the element should be completely absent. The line chosen for vanadium is free from superposition by the lines of any of the other elements

---

* T. Berezina took part in the work.

which may be present in the test samples. Work was carried out with exclusion of the background, for which purpose one of the spectra was photographed with a step-like attenuator for constructing the characteristic curve.

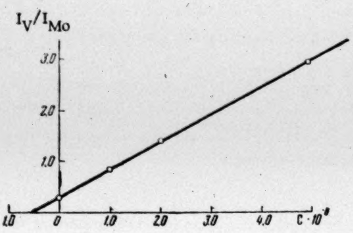


Fig. 1

TABLE 1

Sample no.	Amount of V in the test in g	Content of V in the original ore in %	Mean value of V content in %
1	$0.52\cdot10^{-6}$	0.0104	0.0098
	$0.50\cdot10^{-6}$	0.0100	
	$0.49\cdot10^{-6}$	0.0098	
	$0.50\cdot10^{-6}$	0.0100	
	$0.48\cdot10^{-6}$	0.0096	
2	$0.61\cdot10^{-6}$	0,049	0.0495
	$0.63\cdot10^{-6}$	0.050	
3	$0.10\cdot10^{-5}$	0,020	0.020
	$0.10\cdot10^{-5}$	0.020	
4	$0.38\cdot10^{-5}$	0.076	0,076
	$0,38\cdot10^{-5}$	0.076	

TABLE 2

Ores	V found in %		Difference
	Colorimetrically	Spectrographically	
1	0.0105	0.0099	0.0006
2	0.0485	0.0495	0.0010
4	0.075	0.076	0.001

2) It is essential that the test element should be contained in the original sample in the same form as that in which this same element is added to the test sample. We achieved this condition by clinkering the test sample into a dense compact mass—assay buttons—in the reducing atmosphere of a special carbon electric oven [6]. When this is done, both the vanadium originally contained in a test sample, as well as vanadium added to the sample, are both reduced, apparently to oxides of lower valencies. The test material in the form of a sufficiently stable assay button is transferred onto copper or carbon electrodes, and ignited in the A. C. arc under the conditions chosen. The lower electrode had a cavity 1 mm deep, while the upper electrode was drawn out into a truncated cone with a diameter of 1 mm at the top. It should be noted that the arc operated steadily on the "assay bead" which, as a result of the clinkering process was a sufficiently good conductor of electricity.

Since we obtained good results with our synthetic mixtures we turned to the analysis of ores at our disposal. Silicates containing varying amounts of SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Mn, U, Th, and other elements were analyzed. Since some of the samples at our disposal contained hundredths of a percent of vanadium, and we had made it our aim to achieve high sensitivity, we diluted the ores with copper powder.

Table 1 contains results for a series of determinations; sample No. 1 was analyzed several times. On Fig. 1 is given an example of one curve for ore No. 1.

As is evident from this table, the reproducibility of the method is good enough. In order to confirm the correctness of the proposed spectrographic method for determining small amounts of vanadium, we used a colorimetric method. Colorimetric determinations were carried out on the basis of the phospho-tungstate method on a Type M photoelectric colorimeter, using a blue filter.

Results of spectrographic and colorimetric determinations are compared in Table 2.

A spectrographic analysis, including preparation of sample, takes 8 hours.

Thus, by clinkering the test into an assay bead and using the method of additions it is possible to determine rapidly, with reasonable accuracy and sensitivity by a direct spectrographic method, small amounts of vanadium in natural materials of the silicate type. The determinations are not affected by any amounts of uranium or any of the other components enumerated above.

The authors wish to thank Yu. V. Morachevsky for his advice in the course of the work described here.

LITERATURE CITED

[1] A. M. Shavrin, Factory Lab. 1, 53-56 (1949).

[2] A. M. Shavrin, Bull. Acad. Sci. USSR, Phys. Ser. 5 (1950).

[3] N. V. Buyanov, Bull. Acad. Sci. USSR, Phys. Ser. 4 (1948).

[4] E. N. Lesnikova, Bull. Acad. Sci. USSR, Phys. Ser. 2 (1954).

[5] V. K. Prokofiev, Photographic Methods of Quantitative Spectrographic Analysis of Metals and Alloys (1951), 2.

[6] Zak and Ruvinskaya, Bull. Acad. Sci. USSR, Phys. Ser. 5 (1950).

Received June 8, 1956

BLANK
PAGE

POLAROGRAPHIC REDUCTION OF THE PERMANGANATE ION ON PLATINUM AND MERCURY ELECTRODES

O.A. Songina and Z.B. Rozhdestvenskaya

Kazakh State University, Alma-Ata

The permanganate ion is reduced on the rotating platinum microelectrode [1, 2], the wave starts at about + 1 V (against the saturated calomel electrode), while the diffusion current starts at a potential of +0.6 V.

In developing methods for amperometric titration using permanganate it is essential to know how the composition of the supporting electrolyte, and its acidity, affect the process of permanganate reduction, and in the first instance, the potential of the corresponding current.

The potential at which the permanganate ion is reduced should depend on hydrogen ion concentration, since the value of the oxidation potential of the system MnO_4/Mn^{2+}, is expressed by the equation

$$E = E_0 + \frac{0.058}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

The potential shift with change in hydrogen ion concentration, per pH unit, should amount to $8 \cdot 0.058/5 = 0.093$ V.

Kolthoff [3], studied the relation between the equilibrium potential of the system MnO_4^-/Mn^{2+} and pH, in the region 7 to 0, and got results which were in satisfactory agreement with theory.

All the same, equilibrium potentials differ essentially from potentials when current is flowing. Accordingly, it is impossible to switch over to polarography, results which have been obtained potentiometrically.

In the literature, apart from the articles mentioned above [1, 2], there is very little information about the polarography of the permanganate ion either on mercury or platinum electrodes. Stackelberg and coworkers [4], found that the permanganate ion during electrolysis on a dropping mercury electrode, using barium chloride as supporting electrolyte, gives two waves; nevertheless, these are unsuitable for analytical purposes. Frumkin and Florianovich [5] studied, amongst a number of other anions, the reduction of permanganate on a dropping mercury electrode; they showed that permanganate, in contrast to other ions, does not give a current minimum in the potential region which is negative with respect to the null discharge of mercury.

Rius and Carancio [6] assert that polarographic determination of permanganate on a streaming mercury electrode is not successful on account of the "incorrectness" of the wave.

Positive results were only obtained by a few investigators working with a platinum microelectrode. Thus Kolthoff and Jordan [2], used the wave of permanganate in a supporting electrolyte of 1 M sulfuric acid for titrating iodides. Alimarin and Terin [1], demonstrated the possibility of using permanganate for amperometric titration of tin, antimony, and arsenic in a supporting electrolyte of sulfuric acid (0.1 - 0.5 N).

All the same, the information given in these articles on the polarographic reduction of permanganate is very haphazard and refers only to a few special cases of determinations of individual ions under conditions specially chosen for these cases, in fact in dilute solutions of sulfuric acid. We have studied reduction of permanganate in our laboratory.* Our experiments showed that, in particular, the wave height for reduction of the permanganate ion in sulfuric acid as supporting electrolyte is proportional to its concentration; this is shown by the constancy (within the limits of experimental error) of the value of K in the equation: $i_d = KC$ (see Table).

$KMnO_4$ concentration 10^5	Wave height	$K = \frac{i_d}{C}$
9.1	78	8.55
6.8	59	8.70
4.6	39	8.50

In addition, of practical interest is the possibility of polarography in general, and of permanganate in particular, in more concentrated solutions of sulfuric acid as supporting electrolyte. Thus, for example, Vlcek [7], in carrying out polarographic determinations of thallium and cadmium in concentrated sulfuric acid, showed that 17 N sulfuric acid has a number of advantages as a supporting electrolyte : the electrical conductivity of such a solution is approximately the same as that of 1 N KCl; water, under these conditions in the role of a base, acts as an indifferent electrolyte.

In addition, a study of the effect of the concentration of the supporting electrolyte over wider limits would give one the possibility of getting some general ideas on the behavior of the permanganate ion under conditions of polarographic reduction.

We carried out experiments on the effect of the composition of the supporting electrolyte, and the material of the electrode on the polarographic reduction of permanganate ions in sulfuric acid solutions of varying concentrations; a dropping mercury electrode and a rotating platinum micro-electrode were used.

Current-voltage curves were taken by means of a PPT-1 visual type polarograph, made in the workshops of the Power Institute of the Academy of Sciences, Kazakh SSR, using a mirror galvanometer Type M–21, with a sensitivity of 10^{-9} A/mm.

In experiments with a platinum electrode, the cathode was a platinum wire 0.5 mm in diameter fused into a glass tube; the length of the working part of the electrode was 4 mm. The electrode was rotated by a motor operating at a constant speed of 366 revolutions/minute. The reference electrode was a saturated calomel electrode connected to the electrolyzer via an intermediate flask and bridge filled with a saturated solution of KCl or KNO_3.

Dissolved oxygen was removed before taking polarograms by passing hydrogen through the solution for 20 – 60 minutes; this hydrogen was prepared by electrolysis of 30% alkali solution. When the platinum electrode was used, this operation was unnecessary, since reduction of permanganate ions occurs at potentials which are appreciably more positive than the reduction potential of oxygen.

EXPERIMENTAL RESULTS

In sulfuric acid media, during electrolysis with a platinum electrode, permanganate ions at concentrations of 10^{-3}-10^{-5} N give a clearly defined diffusion current in the potential range +0.2 to 0.6V (with respect to the saturated calomel electrode).

---

*L. S. Makarenko took part in this section of the work

The half-wave potential lies in the limits +0.7 to +0.9 V (Fig 1). Since the resistance of the system did not exceed 2,000 ohms, correction for IR was not more than 0.02-0.03 V. With increasing supporting electrolyte concentration from 2 to 6N, the wave height drops smoothly. At higher sulfuric acid concentrations (within the limits 6 to 10 N) this drop in the wave height becomes appreciably sharper; nevertheless, on further increasing sulfuric acid concentration, there is observed on the contrary, even a certain increase in the value of the diffusion current for permanganate.

Experiments also showed that the way in which the current-voltage curve is taken, other conditions being equal, also affects wave height. When reduction of the permanganate ion was preceded by strong cathodic polarization of the electrode (i.e. if the electrode is polarized first from 0 to -1.0 V, and only after this from 0 to +1.2 V) then the wave height was smaller than when the wave was obtained directly from -0.3 V to +1.2 V (with respect to the saturated calomel electrode).

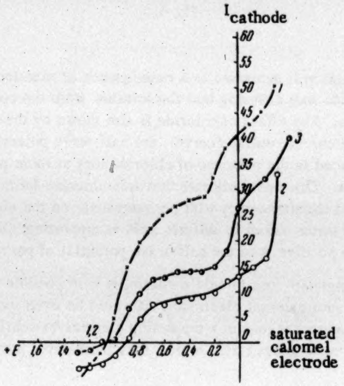


Fig. 1

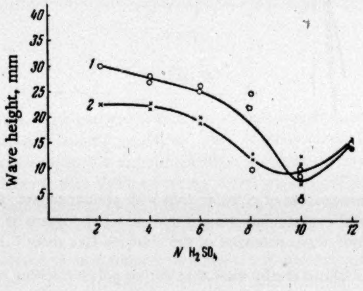


Fig. 2

On Fig. 2 is shown the relation between wave height and sulfuric acid concentration when these two methods of taking the current-voltage curves were used. It is clear that at concentrations of sulfuric acid up to 8 N, both curves are almost parallel, dropping slightly with increasing sulfuric acid concentration. Under these conditions the wave height is reproduced fairly well, just as in 12 N sulfuric acid. At acid concentrations of 8-10 N there is observed a very large scatter of points in a series of parallel experiments, and a sharp drop in wave height; this apparently points to chemical interaction between permanganate and sulfuric acid throughout the whole solution just at these concentrations of sulfuric acid.

Not being in a position at present to explain the reason for the nature of the phenomena described, we shall only point out that we observed a very rapid decolorization of the permanganate solution in 8 - 10 N sulfuric acid in qualitative tests. In 12 N sulfuric acid, decolorization was significantly slower.

The effect of cathodic pre-polarization on the wave height of the permanganate ion can be explained by the action of atomic hydrogen, adsorbed on the surface of the platinum during cathodic polarization, on the permanganate ions. As a result of this, some of the permanganate ions are reduced by hydrogen at the electrode surface, not participating in the electrode process. In the article by Dmitrichev [8], it was shown that hydrogen evolved on metals during their chemical interaction with acid or alkali, also reduces the permanganate. The decrease in the wave height of permanganate may serve as a measure of hydrogen adsorption on the platinum electrode.

During work with a connecting bridge filled with potassium chloride (instead of KNO_3), the effect of cathodic pre-polarization was not observed, while the wave height, for all concentrations of the supporting electrolyte below 6N, independently of the method used for taking the current - voltage curves, was considerably smaller than in experiments with a nitrate bridge. It is obvious that the concentration of permanganate

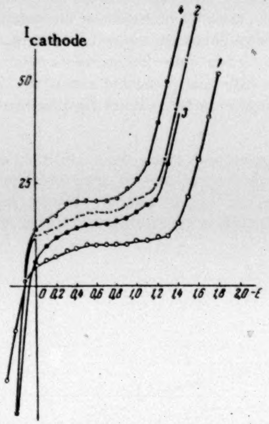


Fig. 3

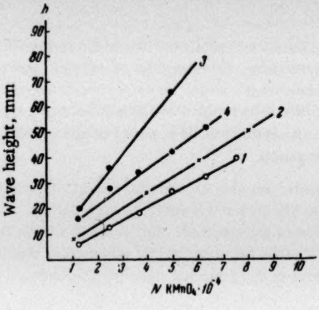


Fig 4.

in solution is depressed as a consequence of reaction with chloride ions diffusing into the solution from the connecting bridge. The effect of chloride is also shown by the shape of the current-voltage curve: the half-wave potential is displaced in the presence of chloride ions to more positive values. This shift indicates that free chlorine formed by the interaction of chloride ions with permanganate is reduced simultaneously with permanganate on the electrode. Special experiments showed that on a polarogram of chlorine water, taken in sulfuric acid as supporting electrolyte, the half-wave potential of the chloride lies about 0.1 V more positive than the half-wave potential of permanganate.

These results show that during polarographing of permanganate ions in acid medium, it is impossible to use a chloride bridge, which is normally used in conjunction with calomel electrodes. It would be even more difficult to get good results when taking polarograms of permanganate ions in a supporting electrolyte consisting of acidfied potassium chloride, as Rius and Carracio [6] (mentioned above) tried to do; they themselves pointed out the unsatisfactory nature of the waves obtained.

During electrolysis of solutions of permanganate (concentrations of the order of 10^{-3}-10^{-5}N) in sulfuric acid, using a dropping mercury electrode, a wave is observed whose limiting current lies in the potential range +0.1 to -1 V (saturated calomel electrode) (Fig. 3).

For all the sulfuric acid concentrations studied (from 0.1 to 12 N) the wave height is proportional to permanganate concentrations in solution (Fig. 4).*

The diffusion current observed during electrolysis of sulfuric acid solutions of permanganate when a dropping mercury electrode is used, is mainly in the region of negative potentials, and at a potential of 0.1 V (against the saturated calomel electrode) it fuses into the oxidation wave of mercury.

This fact suggests that the wave is determined by the reduction current not only of the permanganate, but of mercury ions formed as a result of direct oxidation of metallic mercury by permanganate. This hypothesis is confirmed by the fact that such a wave is also obtained in those cases, where, for sulfuric acid concentrations of 6 - 10 N, there is a very rapid disappearance of the rose color of permanganate during the polarographic process.

---

* R. Kh. Monasypova took part in the experimental work

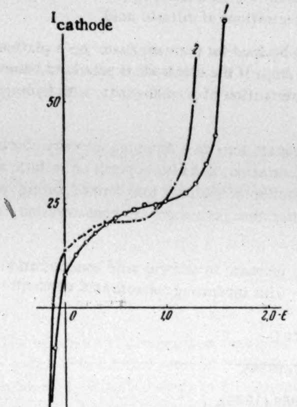


Fig. 5

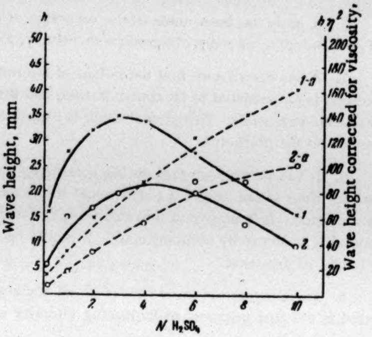


Fig. 6.

In fact, what happens is that the already decolorized solution is polarographed, the wave obtained nevertheless of exactly the same shape, and occupies an identical position to that obtained during polarographing of rose-colored solutions of permanganate in a supporting electrolyte consisting of weaker sulfuric acid.

It is of interest to note that a similar wave is also observed when solutions of potassium dichromate of the same concentrations as the permanganate are polarographed (Fig. 5). Actually, if the wave is determined by reduction of mercury ions which have been formed as the result of the interaction of metallic mercury with an oxidizing agent, then, in the presence of an sufficiently strong oxidizing agent, a wave of this kind should be obtained.

The fact that Frumkin and Florianovich [5], during polarographic study of permanganate, did not observe a minimum current at more negative potentials than that of the null discharge suggests that the wave which arises during electrolysis of permanganate using a dropping mercury electrode, is determined by reduction of the cation (mercury) and not the anion (permanganate).

Direct interaction of the permanganate ion with mercury was confirmed by qualitative tests in the absence of electrolysis, in solutions of varying sulfuric acid concentrations but constant permanganate concentration. In the course of these tests it became clear that in solutions whose sulfuric acid concentrations were 8-10 N, decolorization proceeds particularly quickly, incomparably faster than in the absence of mercury.

The relation between wave height for reduction of mercury ions formed during interaction with permanganate ions and sulfuric acid concentrations is shown in Fig. 6. The nature of this relationship is apparently determined, on the one hand, by the effect of hydrogen ion concentration; and on the other, by the viscosity of the medium. Introduction of corrections for viscosity changes makes this relation almost linear (Curves 1a and 2a, Fig. 6).

The fact that the height of this characteristic "permanganate" wave is proportional to permanganate concentration over a wide concentration range of sulfuric acid gives a basis for reckoning that it should be possible to estimate the concentration of permanganate in solution on the basis of the height of this wave (in the absence of other oxidizing agents capable of oxidizing mercury).

SUMMARY

1. A study has been made of the reduction of the permanganate ion on a rotating platinum electrode, and on a dropping mercury electrode, respectively, at various concentrations of sulfuric acid.

2. It has been shown that the height of the reduction wave obtained for permanganate on a platinum electrode is proportional to its concentration, and that this height drops if the electrode is polarized beforehand at negative potentials. This phenomenon is explained by direct interaction of permanganate with hydrogen adsorbed on the platinum.

3. It has been shown that during polarographing of permanganate ions on a dropping mercury electrode, a wave develops whose height is proportional to permanganate concentration, and also depends on sulfuric acid concentration. It is suggested that this wave is determined by reduction of mercury ions formed during oxidation of metallic mercury by permanganate. It should be possible to determine permanganate concentration from the height of this wave.

4. The decrease in wave height which accompanies a large increase in sulfuric acid concentration is related, in the first instance, to increasing viscosity of the solution with increasing sulfuric acid concentration.

LITERATURE CITED

[1] I.P. Alimarin and S.I. Terin, Factory Lab. 20, No. 1, 18 (1954).

[2] J.M. Kolthoff and J. Jordan Anal. Chem. 25, No. 12, 1883 (1953).

[3] I.M. Kolthoff and N. Fourman, Potentiometric Titration (United Sci.-Tech. Press, Leningrad, 1935).

[4] M. von Stackelberg, P. Klinger and W. Koch, Forschungsber. Tech. Mitteilungen, Krupp., Essen. 2, 59 (1939); cited from I.M. Kolthoff and D. Lingane in Polarography (State Chem. Press, Moscow, 1948).

[5] A.N. Frumkin and G.M. Florianovich, Proc. Acad. Sci. USSR 80, No. 6, 907 (1951).

[6] A. Rius, H. Carrancio, Anales real. soc. espan. fis. y quim. 47 B, 379.

[7] A.A. Vlcek, Sbornik mezinarod. polarogr. sjezdu praze 3, 370, (1951); cited from C. A. 47, 11030 (1953).

[8] A.K. Dmitriev, J. Gen. Chem 22, No. 4, 545 (1952) (T.p. 611).*

Received February 12, 1955

---

* T.p. = C.B. Translation pagination.

DETERMINATION OF VERY SMALL AMOUNTS OF NITRATE, NITRITE, AND HYDROXYLAMINE

N. S. Drozdov and A. K. Iskandaryan
Second Moscow Medical Institute

The necessity of determining very small amounts of nitrate, nitrite, and hydroxylamine, when all are present together in solution arose in connection with studies on nitrogenous metabolism in plants, particularly in bacteria, and during the study of the nitrogen cycle [1]. Further, a reasonably sensitive, accurate, and rapid method of determining nitrate, nitrite, and hydroxlylamine is also necessary for solving a number of technological questions [2].

Griess' method has long been in use for qualitative and quantitative determination of nitrite [3]. This method is based on the reaction of nitrite in acid media with sulfanilic acid to form a diazo compound which is then coupled with an aromatic amine. The amine usually used is α-naphthylamine [4] which forms the azo dye benzenesulfonic acid-1-4-azo-4-naphthylamine-1; this has a red color in acid solution the color change occurs in the pH range 3.5-3.7).

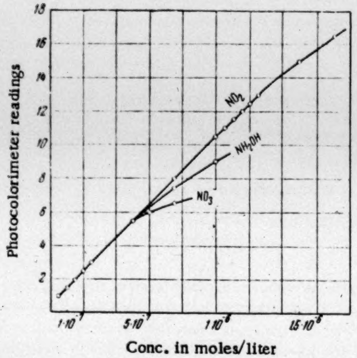
Blom [5], suggested a method for qualitative detection of hydroxylamine which was based on oxidation of hydroxylamine in acid media with iodine, and detection of the nitrous acid formed by means of the Griess reaction. In the same paper, Blom showed that nitrates can also be qualitatively detected by means of the Griess reaction after reduction with zinc. Blom developed a method for the qualitative detection of nitrate, nitrite, and hydroxylamine when they are all present together.

The sensitivity of nitrate detection, as Blom pointed out, when such a method is used, is considerably lower than the sensitivity of the method for detecting hydroxylamine and nitrite, because of reduction of the azo dye by zinc. As for detection of hydroxylamine, then, according to Blom's results [6], his method is more sensitive than any other method for qualitative detection of hydroxylamine [7].

An attempt to use the Griess-Blom method for quantitative determination of nitrates was made by Lemoigne, Monguillon, and Desveaux [8], who used reduction of nitrate with zinc, and subsequent reoxidation of the reduction products to nitrous acid. Using this method, they claim that it is possible to determine 0.14-1.40 mg of nitrate nitrogen with a fair degree of accuracy in 1 liter of test solution, or, taking into account the dilution, to determine nitrite at 10^{-5}-10^{-4}M in the liquid which is measured colorimetrically.

All the same, on verifying this method of determination for nitrates, Haag and Dalphin [9] showed that, using the conditions specified, quantitative conversion of NO_3^- to NO_2^- is not observed, and that the length of time for which reduction with zinc is carried out, and NO_3 concentration, affect the experimental results. According to the results of these authors, nitrate can be determined fairly accurately only when NO_3^- concentration in the liquid being measured colorimetrically does not exceed 10^{-6} mole/liter.

Similar results were published by White [10], who also detected considerable inaccuracies in the method of Lemoigne, Monguillon, and Desveaux for determining nitrate, and indicated that this method could only be used for qualitative detection.



Endres and Kaufman[11] worked out a quantitative method for determining small amount of nitrate, nitrite, and hydroxylamine. For nitrate determination they suggested colorimetric measurements based on the color formed during reaction of nitrates with brucine [12]. They only used the Griess - Blom reaction with subsequent photometric determination of the color of the azo dye for determining nitrite and hydroxylamine.

These authors found that on using this method they could determine nitrite and hydroxylamine with an error of ~ 2-3% at concentrations of 10^{-6}-10^{-5} M/liter; according to their results, at such concentrations there is a linear relation between extinction and nitrite or hydroxylamine content, respectively, in the test solution; i.e. the color developed obeys the Lambert-Beer law at these concentrations. They believe that only at concentrations higher than $2 \cdot 10^{-5}$ M/liter does one get inaccuracies as a result of the poor solubility of the azo dye.

As for photometric determination of nitrate with brucine, then here, according to their results, the sensitivity is at least ten times less than that for determination of nitrite and hydroxylamine.

In the work described here we have developed a quantitative method of determining nitrate, nitrite, and hydroxylamine, based on photometric measurements of the color of the azo dye formed during the Griess-Blom reaction. In this method the nitrite is determined directly in the test solution, since the presence of nitrate and hydroxylamine does not interfere with its accurate determination. To determine nitrite fairly accurately, a number of conditions has to be observed. Mineral acids affect the accuracy; accordingly, determinations must be carried out in acetic acid media. All reagents should be carefully checked for absence of traces of nitrite. In addition, our experiments showed that the linear relation between the intensity of the color developed and nitrite concentration in solution is only observed at concentrations below $1.2 \cdot 10^{-6}$ mole nitrate/liter of solution being measured colorimetrically. At higher concentrations (see diagram) there is an appreciable deviation from linearity, and the color developed does not obey the Lambert-Beer law. Therefore, accurate determination of nitrite is only possible at concentrations less than 10^{-6} mole of nitrite/liter of solution being measured colorimetrically.

As can be seen from our results, the permissible nitrite concentration for accurate determination is appreciably lower than that indicated in the work of Endres and Kaufman.

For subsequent determination of hydroxylamine, the test solution should be free from nitrite. Methods based on reactions with ammonium salts, with urea, or azide are not very suitable since they do not guarantee rapid and sufficiently complete removal of HNO_2, and do not exclude the possibility of side reactions leading to loss of hydroxylamine and formation of HNO_3.

Drawbacks of this type are also characteristic of the method proposed by Endres and Kaufman; they include breakdown of nitrous acid via diazosulfanilic acid on heating the latter with sodium azide. Apparently, mainly as the result of this drawback of the method used for removing HNO_2, determination of hydroxylamine, according to the method of Endres and Kaufman (as the authors themselves point out) leads to errors of 10%.

In the method described in this article, we converted the nitrous acid into diazosulfanilic acid, which was then heated; it broke down completely to give gaseous nitrogen.

This method of removing HNO_2 does not lead to any complications during subsequent determination of hydroxylamine.

After removal of nitrite from solution by the method just indicated, the hydroxylamine is oxidized by iodine to nitrous acid in the presence of sulfanilic acid (Bloom's reaction). Excess iodine is removed with thiosulfate. The diazonium salt formed is coupled with α-naphthylamine and the color of the azo dye measured photocolorimetrically. The linear relation between intensity of the color developed and hydroxylamine concentration only holds for solutions whose concentration of hydroxylamine is less than 5.10^{-7} M/liter (see diagram).

At higher concentrations considerable deviations are observed from linearity.

It follows that accurate determination of hydroxylamine is possible only at much lower concentrations than those indicated by Endres and Kaufman.

Nitrate can be determined only after removal of nitrite and hydroxylamine from the test solution. This last is achieved by the action of sulfanilic acid in acetic acid solution plus addition of iodine, after which the diazonium compound formed is destroyed by heating.

After removal of nitrite and hydroxylamine, nitrate is reduced with zinc dust in the same acetic acid solution. Various reduction products are formed during this stage (up to hydroxylamine inclusively) which are further re-oxidized to NO_2^- by the action of iodine in acetic acid in the presence of sulfanilic acid. The diazosulfanilic acid formed is coupled with α-naphthylamine and the color measured.

As our experiments showed (see diagram), the linear character of the relation between intensity of the color of the azo dye formed and nitrate concentration of the solution is only maintained at nitrate concentrations below $5 \cdot 10^{-7}$ M/liter. From this it is obvious that nitrate can only be determined with a reasonable degree of accuracy at concentrations of $5 \cdot 10^{-8} - 5 \cdot 10^{-7}$ M/liter, i.e. at concentrations which are one thousandth of those indicated in the work of Lemoigne, Monguillon, and Desveaux [1].

Chloride ions affect the intensity of the color of the azo dye formed, and consequently affect the accuracy of determination of nitrate, nitrite, and hydroxylamine. Thus in the presence of 0.25% sodium chloride in the test solution, the error in determining nitrite may be 20% on the high side. Nevertheless, this error, which is determined by the presence of chloride ions, can easily be eliminated by strong dilution of the solution. Thus, on diluting the solution containing 0.25% NaCl 100 times, chloride ions no longer have an appreciable effect on accuracy of determination. Such considerable dilutions are permissible and do not interfere with the quantitative determination of nitrate, nitrite, and hydroxylamine when the method which has been worked out is used, because of the very high sensitivity of the latter.

Necessary Reagents. 1. Sulfanilic Acid Solution (0.05 N). 10.5 g of sulfanilic acid, 6.8 g of sodium acetate ($CH_3COONa \cdot 3H_2O$) and 300 g of glacial acetic acid are heated with 600 ml of water to the boil; the mixture is boiled for 3 minutes, cooled, and made up to 1000 ml.

2. α-Naphthylamine Solution (0.035 M). ~ 1000 ml of water is heated to the boil and 5 g of α-naphthylamine added, and the whole boiled for 5 minutes. The mixture is filtered, and to the hot filtrate is added 5 ml of concentrated hydrochloric acid (sp. gr. 1.19), ; after cooling, the volume is made up to 1000 ml.

3. Iodine Solution (~ 0.1 N) 1.3 g of iodine is dissolved in 100 ml of glacial acetic acid.

4. Thiosulfate Solution (0.1 N). 2.5 g of thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) is dissolved in 100 ml water.

5. Zinc dust. Zinc dust is purified from traces of nitrate and nitrite by heating it, with stirring, on a water bath with twice its volume of 20% acetic acid for 1 hour.

On cooling, it is filtered off and washed first with 20% acetic acid, and then with water till the washings give a neutral reaction; it is finally dried at 65°.

6. Water should be completely free from traces of nitrate and nitrite.

Experimental Procedure. For nitrite determination 10 ml of test solution is placed in a 100 ml standard flask, 25 ml water added, followed by 1 ml of the 0.05 M solution of sulfanilic acid (Solution 1).

The contents of the flask are mixed and left to stand at room temperature for 15-20 minutes; 1 ml of 0.035 M α-naphthylamine solution is then added (solution 2), the whole mixed, and then after standing for 20 minutes, the volume made up to 100 ml. The color is measured photocolorimetrically and nitrite concentration found from the standard curve (see diagram).

For determination of hydroxylamine, 10 ml of test solution is placed in a 100 ml flask, and 25 ml water is added followed by 0.5 ml of 0.05 M sulfanilic acid (solution 1). The mixture is heated on a boiling water bath for 5-6 minutes and then cooled to room temperature.

After cooling, 1.5 ml of sulfanilic acid solution 1 is added to the solution thus obtained, followed by 1 ml of ~ 0.1 N iodine solution (solution 3). After 5 minutes excess iodine is removed by addition of sodium thiosulfate solution (solution 4) until the iodine color disappears. After standing for 5 minutes, 1 ml of α-naphthylamine solution (solution 2) is added and the whole mixed; after a period of 20 minutes the volume is made up to 100 ml with water, and the color of the azo dye is measured.

Nitrate is determined as follows: 10 ml of test solution is introduced into a 20 ml graduated test tube, 0.3 ml of 0.05 M sulfanilic acid (solution 1) is then added, followed by 0.2 ml of ~ 0.1 N iodine solution (solution 3). After 5 minutes, the whole is heated on a boiling water bath for 5-6 minutes; the contents are cooled and the volume made up to 20 ml. The test tube is next placed in melting ice for 15-20 minutes, and without taking the tube out of the ice, ~ 1 g of zinc dust, purified as described above, is added.

Reduction is complete in 15-30 seconds.

The zinc dust is filtered off and 10 ml of the filtrate obtained transferred to a 100 ml standard flask; 25 ml of water is added, followed by 2 ml of 0.05 M sulfanilic acid and 1 ml of ~ 0.1 N iodine solution (solution 3) and the whole left for 5 minutes. Excess iodine is removed by addition of sodium thiosulfate solution (solution 4) until the iodine color disappears. After 5-6 minutes, 1 ml of 0.035 M α-naphthylamine solution is added, the whole left to stand for 20 minutes, when the volume is made up to the mark with water and the color measured.

A blank is carried out in all cases in parallel with the test, distilled water being used instead of test solution.

Results for determination of nitrate, nitrite, and Hydroxylamine are given in the table. In these experiments test solutions which had been analyzed beforehand were diluted to the concentration at which they were analyzed by the method described above.

SUMMARY

1. A method has been developed for the quantitative determination of very small amounts of nitrate, nitrite, and hydroxylamine when they are all present together in solution; the method is based on photocolorimetric determination of the color of the azo dye formed during the Griess reaction.

2. It has been established that nitrite can be determined quantitatively without removal of nitrate and hydroxylamine, at concentrations not exceeding $1.2 \cdot 10^{-6}$ mole of nitrite/liter of solution being colorimetrically measured.

3. After removal of nitrite as gaseous nitrogen from the solution by conversion through the diazosulfanilic acid, hydroxylamine is oxidized by iodine in the presence of sulfanilic acid (Blom's reaction), excess iodine is removed, the diazosulfanilic acid formed is then coupled with α-naphthylamine and the color of the dye formed is measured photocolorimetrically. Accurate determination by means of this method is only possible at hydroxylamine concentrations less than $5 \cdot 10^{-7}$ M/liter in the solution whose color is measured.

4. Nitrate is determined by removing nitrite and hydroxylamine from solution by the action of iodine in acetic acid solution in the presence of sulfanilic acid, and subsequent break down of the diazosulfanilic acid by heating.

5. After removal of nitrite and hydroxylamine from solution nitrate is determined by reduction with zinc dust in acetic acid solution and subsequent re-oxidation of the reduction products. It is possible in this way

to determine nitrate as long as the concentrations are less than $5 \cdot 10^{-7}$ Mol. of nitrate/ liter of the solution whose color is being measured.

TABLE

$NaNO_2$ in g/1000 ml		$NH_2OH \cdot HCl$ in g/1000 ml		$NaNO_2$ in g/1000 ml	
Taken	Found	Taken	Found	Taken	Found
0.500	0.502	0.200	0.196	5.00	4.96
	0.505		0.203		4.98
	0.506		0.198		4.95
0.200	0.198	0.500	0.500	2.50	2.51
	0.203		0.493		2.50
	0.202		0.492		2.52
0.100	0.102	0.100	0.096	2.00	1.98
	0.101		0.098		1.98
	0.098		0.100		1.99

LITERATURE CITED

[1] M. Lemoigne and R. Desveaux, Bull. soc. chim. biol. 18, 604 (1936); M. Lemoigne, P. Monguillon, and R. Desveaux, Bull. soc. chim. biol. 18, 841, 868, 1291 1297 (1936); Compt. rend 204, 1841 (1937; G. Endres and L. Kaufmann, Ann. 512, 54 (1934); 518, 109 (1935).

[2] N.S. Drozdov and A.K. Iskandaryan, Meat Ind. USSR 6, 24 (1953).

[3] P. Griess, Ber. 12, 427 (1879).

[4] Ilosvay von Ilsova , Bull chim. soc. (3) 2, 317.

[5] J. Blom, Ber. 59, 121 (1926).

[6] J. Blom, Biochem. Z. 194, 385 (1928).

[7] M. Lemoigne, P. Monguillon and R. Desveaux, Bull. Soc. chim. biol. 18, 841 (1936).

[8] M. Lemoigne, P. Monguillon and R. Desveaux, Compt. rend 204, 689 (1937).

[9] E. Haag and C. Dalphin, C. 11, 677 (1944).

[10] W. White, Can. J. Research 17, 6, 125 (1939).

[11] G. Endres and L. Kaufmann, Ann. 530, 184 (1937).

[12] C. Urbach, Mikrochemie 10, 483 (1931).

Received January 16, 1955

BLANK
PAGE

SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN, AND SULFUR IN ORGANIC MATERIALS

N. V. Sokolova

Institute of High Molecular Weight Compounds Academy of Sciences, USSR

During simultaneous determination of carbon, hydrogen, and sulfur in organic compounds by means of Korshun and Sheveleva's method [1], after decomposition of the organic compound, the sulfur is converted into a mixture of oxides in an oxygen atmosphere. These oxides are quantitatively trapped with heated silver in the form of Ag_2SO_4. In these determinations the silver is placed in a separate, tared quartz apparatus which is connected via a ground glass joint to the end of the combustion tube.

We used silver of 99.99% purity in the form of pieces of foil 0.06 mm thick. Tests showed that in this form, silver rapidly lost its activity and ceased to absorb the sulfur oxides quantitatively. E.g., 5.23 g of silver foil was placed in the apparatus. 24 combustions were carried out with this filling. When it was used for more determinations, low results for sulfur were obtained. The silver was washed with boiling water until it gave a negative reaction for SO_4^{2-}. The wash liquor was found to contain 58.8 mg of SO_4 (as $BaSO_4$) which corresponded with 132 mg of Ag. Thus, of all the silver taken, only $\frac{0.132}{5.23} \cdot 100 = 2.48\%$ Ag reacted with the sulfur oxides. In order to increase the efficiency of the silver we used silvered pumice.

For micro-analysis we used silver deposited on pieces of unglazed clay plates [2], with small surfaces.

Preparation of Silvered Pumice

Pumice was ground to give particle sizes of 2-3 mm; it was sieved free of dust and treated by boiling with 10% nitric acid, followed by a few portions of 10% hydrochloric acid until the acid extracts of the pumice were colorless, indicating completion of removal of impurities soluble in acid from the pumice; it was finally washed several times with boiling distilled water until a negative chloride reaction was obtained; it was then dried at 100°-120° and calcined in a crucible oven for 30 minutes at 800°.

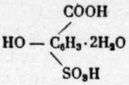
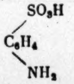
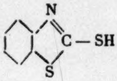
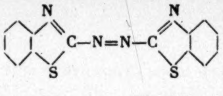
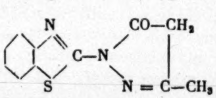
The pumice was next covered in a porcelain crucible with a 20% solution of silver nitrate (2 ml of 20% $AgNO_3$/ g of pumice). After 24 hours the solution was evaporated first on a hotplate and finally in a drying oven at 100-120°. After drying, the pumice was calcined in a crucible oven at 800° for 30-40 minutes until oxides of nitrogen disappeared. The treatment with silver nitrate was repeated once again. For this twofold treatment the total amount of silver nitrate used was 80% of the weight of pumice, or—calculated in terms of metallic silver—50.4%. After treatment the pumice had a silvery grey color.

Determination of the Silver Content of the Preparation Obtained

Analysis was carried out as follows : an exact amount of ground pumice was treated at the boil with 10% nitric acid, and, after cooling the nitric acid extract was titrated with 0.1 N ammonium thiocyanate in the presence of ferric alum. On repeating the nitric acid treatment of the pumice with nitric acid, no silver was found in the extract. The preparation obtained as described above contained 40.32% Ag.

TABLE

Determination of Sulfur in Organic Materials from Increase in Weight of Silver

Sample designation	Formula	Weight of sample in mg	SO_4^{2-} as der'd by wt. increase of silvered pumice	S content in %		Deviation from theory
				Found	Calculated	
β-naphthalene sulfonic acid	$C_{10}H_7SO_3H \cdot 3H_2O$	6.950	2.580	12.36	12.21	+0.15
		3.730	1.370	12.09		—0.12
		5,985	2.465	12.07		—0.14
		4.740	1.740	12.25		+0.04
		3.470	1.270	12.21		0
Sulfosalicylic acid	 $HO-C_6H_3(COOH)(SO_3H) \cdot 2H_2O$	5,710	2.110	12.30	12.59	—0.29
		5.725	2.110	12,30		—0.29
Sulfanilic acid	 $C_6H_4(SO_3H)(NH_2)$	4.530	2.480	18.28	18.48	—0.20
		4.280	2.330	18,17		—0.31
Thiourea	$CS(NH_2)_2$	3,910	4.920	42.00	42.10	—0.10
		3,750	4.735	42,14		+0.04
Mercaptobenzthiazole (Captax)		3.640	4.155	38.10	38.27	—0.17
		3.525	4.032	38.18		—0.09
Azobenzthiazole		3.410	2.220	21.73	21.62	+0.11
		3,935	2,535	21.50		—0.12
		3.460	2.230	21.51		—0.11
Benzthiazole methylpyrazolone		3.430	1.425	13.87	13.85	+0,02
		4.900	2,005	13.66		—0.19
		4.940	2.045	13,82		—0.03
	$C_{20}H_{22}O_5S_2$	3,385	1.525	15.04	15.75	—0.71
		5.840	2.695	15.40		—0.35
	$C_{29}H_{34}O_{10}S_2$	3,300	1.060	10.97	10.56	+0.41
		3.700	1,190	10,74		+0.18
	$C_{30}H_{34}O_{11}S_2$	3,210	0.980	10.23	10,00	+0.23
		3.730	1.115	9.98		—0,02
	$C_{16}H_{24}O_8S_2$	3.250	1.520	15.61	15.68	—0.07
		4.025	1.905	15,79		+0.11

Pumice which has been silvered by the method described above has been used for trapping sulfur oxides during determination of sulfur in organic compounds by Korshum and Sheveleva's method [1]. Into the quartz apparatus which is connected via a ground-glass joint to the combustion tube was placed 2.42 g of silvered pumice containing 975.7 mg of Ag. This amount of silver can be used for combining with 434.3 mg of SO_4^{2-} (at temperatures from 650°-700°).

Determination was carried out exactly as laid down by Korshun and Sheveleva. When combustion was complete, the apparatus used for absorbing carbon dioxide and water was switched off, the oven used for heating the apparatus containing silvered pumice was removed, and the pumice allowed to cool in an oxygen stream for 10 minutes; the apparatus containing pumice was then disconnected, stoppered with a ground-glass stopper, wiped with chamois, passed through a burner flame, kept for 10 minutes outside the balance, then for 10 minutes in the balance, and finally weighed on an MA-20 micro-balance. The absorption apparatus was weighed before analysis and a blank carried out.

Results for determination of the sulfur content of various organic compounds are given in the table.

This table only contains the results for sulfur, though in all cases carbon and hydrogen were also determined at the same time.

Altogether with this one charge of silvered pumice, 96 combustions were carried out of organic compounds whose sulfur content varied from 6.0 to 65%. As a result of absorption of sulfur oxides, the gain in weight of the silvered pumice was 281.7 mg; consequently, the percentage efficiency of the silver on pumice was 64.80%.

During subsequent combustions the apparatus increased in weight, but quantitative absorption of sulfur oxides did not occur, and in most cases the results obtained were low. E.g., during successive determinations of the sulfur content of mercaptobenzthiazole, the theoretical sulfur content of which is 38.3%, the results obtained were 34.34, then 32.80, and finally 18.20%.

In order to check on the amount of sulfur held by the silver, the pumice from the apparatus was washed with small portions of boiling distilled water until a negative reaction for SO_4^{2-} was obtained (~ one and one half liters of water); sulfate ions were then determined by precipitation with barium nitrate in nitric acid solution. 770 mg of $BaSO_4$ was found, which corresponded to 317 mg SO_4^{2-} and 713 mg of combined silver. The amount of unused silver remaining on the pumice was thus 262 mg. The percentage efficiency of silver as an absorber for sulfur oxides was therefore 64.80%. After washing off the silver sulfate, the pumice was again treated with silver nitrate and recharged into the apparatus.

By using silvered pumice, owing to its porosity the metallic silver is distributed over a very large surface, which favors more complete use of it for reacting with sulfur oxides (64.8% instead of 2.5%).

Because of the small specific gravity of pumice (~ 0.4), an apparatus filled with silvered pumice weighs less than one containing metallic silver, thereby increasing the accuracy of determination of small amounts.

After use, the silvered pumice is readily freed from Ag_2SO_4 and can be used again for deposition of silver on it. Silver foil after use becomes brittle and loses its activity.

SUMMARY

The use of silvered pumice for absorption of sulfur oxides during gravimetric determination of sulfur in organic compounds, by combustion in a quartz apparatus in an oxygen stream, has several advantages over metallic silver.

LITERATURE CITED

[1] M.O. Korshun and N.S. Sheveleva, J. Anal. Chem 7, 2, 104 (1952) (T.p. 121).*.

[2] M. O. Korshun and N. E. Gelman, New Methods of Elemental Microanalysis (Moscow-Leningrad, State Chem. Press, 1949), pp. 29, 103.

Received July 26, 1955

---

* T.p. = C. B. Translation pagination.

BLANK
PAGE

POTENTIOMETRIC METHODS OF INVESTIGATING HIGH MOLECULAR WEIGHT PETROLEUM COMPOUNDS

PART 2. A POTENTIOMETRIC METHOD OF DETERMINING SAPONIFICATION NUMBERS IN SOLUTIONS OF PETROLEUM RESINS *

S. R. Sergienko, P.N. Galich, N. A. Izmailov, and L. L. Spivak

Academy of Sciences, USSR Institute of Petroleum and

Kharkov State University

In a previous article [1], a method was described for the potentiometric determination of acid numbers. Continuing the work on developing methods for potentiometric determination of functional groups in solutions of petroleum resins, products obtained during processing of petroleum, and heavy petroleum ends, we have developed a potentiometric method of determining saponification numbers in solutions of petroleum resins.

Saponification is usually carried out by a widely used method [2] based on the use of alcoholic KOH solution. In the first stage the problem was to increase the accuracy of determination by substituting a potentiometric method for indicator titration, without essentially changing the method itself, and the conditions for determining saponification numbers. Methods have been published for determining saponification numbers potentiometrically [3]. In these methods benzene is used as solvent, while the saponifying solution is a solution of KOH in isopropanol.

Test showed that isopropanol can be succesfully replaced by the more readily available ethanol, which is far easier to purify. The azeotrope of ethanol with water only contains 4% water, so that it will give homogenous solutions; the azeotrope of isopropanol with water, on the other hand, contains an appreciable amount of water which may lead to formation of layers in the system. It would appear also that titration conditions in ethanol-benzene mixtures should be more favorable than in isopropanol-benzene mixtures, since the dissociation constant of the acids will be higher in the former. Further, it would appear to be expedient to use the same aliquot both for determining acid numbers, and for determining saponification numbers, while potentiometric titration of a benzene solution of the petroleum product without addition of a hydroxyl-containing solvent, even when a powerful amplifier is used, is out of the question.

In developing a method, we used individual synthetic esters, petroleum resins, and resins to which had been added individual esters.

EXPERIMENTAL

An aliquot of the material to be saponified was dissolved in a mixture of ethanol and benzene, taken in the ratio of 2:5. To the solution thus obtained was added 5-10 times its amounts of an alcoholic solution of 0.1 N KOH.

The flask and its contents were then connected to a reflux condenser fitted with a ground, glass joint and heated on a water bath for 1 hour. Excess alkali and even heating ensure a more rapid and complete saponification.

---

* For Part 1 see J. Anal. Chem. 10, 315 (1955).

Excess alkali was then titrated with hydrochloric acid solution. Despite the fact that during all the time it was being saponified, the substance was kept close to the boiling point, it was necessary to protect the solution from CO_2. The reflux condenser was accordingly fitted with a soda-lime guard tube. It is also essential to protect the solution from CO_2 during titration; this is achieved by bubbling nitrogen through the solution kept in a carefully sealed vessel.

Titration was carried out on an LP-5 glass and calomel electrodes set-up. The smooth platinum electrode which we used for determining acid numbers and was operating as an oxygen (or air) electrode was inapplicable here, because of the poor solubility of the gas at the high temperature; the quinhydrone electrode was also unsuitable, since titration starts off in a strongly alkaline medium. The potential of the glass electrode is rapidly established and is readily reproducible. Titration was carried out with a 0.1 N alcoholic solution of HCl. Titration curves have the shape shown in Fig. 1.

TABLE 1

Determination of Saponficiation Numbers of Ethyl Isobutyrate and Ethyl Benzoate

Ethyl Isobutyrate			Ethyl Benzoate		
Weight of sample in g	Saponifi-cation in %	Deviation in %	Weight of sample in g	Saponifi-cation in %	Deviation in %
0.0257	100.0	0	0.0237	101.5	+1.5
0.0180	101.0	+1.0	0.0322	99.8	—0.2
0.0181	100.5	+0.5	0.0351	99.2	—0.8
0.0178	98.3	—1.7	0.0116	97.0	—3.0

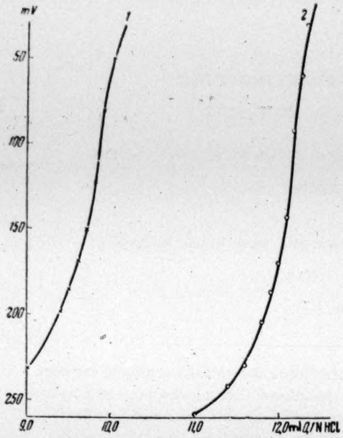


Fig. 1. Titration curves : 1) 0.0271 g of ethyl isobutyrate; 2) blank

Titration with aqueous HCl has an essential drawback: as titration proceeds, the system changes from a homogeneous to a heterogeneous system consisting of two layers; this leads to certain nonreproducibility of the potential and to slow establishment of equilibrium. When excess alkali is titrated with alcoholic HCl, the system remains homogeneous and the potential is more readily reproducible.

Tables 1, 2, 3, and 4 contain results obtained during saponification of ethyl isobutyrate and ethyl benzoate, and also during saponification of Sagaidaksky petroleum resins when alcoholic HCl was used for back titration. It should be noted that the use of alkali contaminated with carbonates leads to a rather diffuse potential jump which is more difficult to determine. The procedure adopted for determining saponification and acid numbers, respectively, in the same sample was as follows.

Acid number was first determined in the dissolved aliquot by the method described in our previous communication [1]; the electrode and stirrer were then removed, any solution washed off them with small amounts of solvent (5 ml) and, after addition of excess alkali, the saponification number determined as described above.

TABLE 2

Determination of Saponification Numbers of Sagaidaksky Petroleum

CCl_4 fraction not soluble in phenol			Benzene fraction soluble in phenol		
Weight of resin in g	0.1 N HCl used for titration in ml	Saponification number in terms of mg of KOH	Weight of resin in g	0.1 N HCl used for titration in ml	Saponification number in terms of mg of KOH
0.1792	0.18	5.6	0.1567	0.38	13.6
0.3066	0.34	6.2	0.1909	0.48	14.1
0.1361	0.15	6.2	0.1447	0.38	14.8
0.1955	0.21	6.0	0.2067	0.54	15.1

TABLE 3

Determination of Saponification Numbers of Ethyl Isobutyrate and Ethyl Benzoate in Mixtures with Benzene Fractions, Sagaidaksky Petroleum Resin Soluble in Phenol

Ethyl Isobutyrate				Ethyl Benzoate			
Weight of sample in g		Saponification in %	Deviation in %	Weight of sample in g		Saponification in %	Deviation in %
Resin	Ester			Resin	Ester		
0.1733	0.0224	98.9	—1.1	0.1378	0.0394	105	+5.0
0.1883	0.0333	100.0	0	0.1698	0.0346	104	+4.0
0.1101	0.0292	101.0	+1.0	0.1118	0.0173	100.8	+0.8
0.1202	0.0308	102.0	+2.0	0.1428	0.0515	97.6	—2.4

TABLE 4

Determination of the Saponification Values of Ethyl Isobutyrate and Ethyl Benzoate in their Mixtures with Carbon Tetrachloride fraction Resin from Sagaidaksky Petroleum Insoluble in Phenol

Ethyl Isobutyrate				Ethyl Benzoate			
Weight of sample in g		Saponification in %	Deviation in %	Weight of sample in g		Saponification in %	Deviation in %
Resin	Ester			Resin	Ester		
0.1788	0.0421	102.8	+2.8	0.1755	0.0524	101.5	+1.5
0.2078	0.0481	99.6	—0.4	0.1379	0.0350	102.8	+2.8
0.2002	0.0309	101.0	+1.0	0.1400	0.0442	96.5	—3.5
0.1587	0.0354	102.0	+2.0	0.1319	0.0352	100.2	+0.2

Calculations were made on the basis of the usual formulas.

SUMMARY

1. On the basis of a detailed study of the effect of the medium, and the conditions of potentiometric titration for determining saponification numbers, a modified method of carrying out the potentiometric titration is suggested. An ethanol solution of HCl is used instead of an aqueous solution for titrating excess alkali, while the solvent used for titrating the samples is an ethanol-benzene mixture (2:5).

2. The method developed permits one to get satisfactory, readily reproducible results for the cases of individual esters and for petroleum resins.

LITERATURE CITED

[1] S.R. Sergienko, N.A. Izmailov, L.L. Spivak and P.N. Galich, J. Anal. Chem. 10, 315 - 322 (1955). (T.p. 299).*

[2] All-Union State Standard 6764 - 53.

[3] ASTM Bull., "Standards petroleum products and lubricants (with related information)" (Nov., 1952).

Received December 27, 1955.

---

* T.p. = C. B. Translation pagination.

TITRIMETRIC DETERMINATION OF ALIPHATIC AND AROMATIC AMINES WITH SODIUM TETRAPHENYLBORON*

A. F. Ievinsh and E. Yu. Gudrinietse

Latvian State University, Riga

Sodium tetraphenylboron has found wide use for determination of potassium and ammonium. But although Wittig and coworkers [1], who were the first to synthesize this reagent, have already pointed out that it gives a precipitate with amines, no systematic work has been carried out hitherto along this direction. Meanwhile there have been a few suggestions published [2, 3, 4, 5, 6], on the use of this reagent for determination of organic nitrogen-containing materials (alkaloids, anaesthetics, pyrazolone derivatives,etc.). Neu [7], has tried it for determining triethanolamine. Since determination of amines is of practical importance, we carried out some experiments on the use of sodium tetraphenylboron for qualitative and quantitative determination of several amines.

Sodium tetraphenylboron forms fine crystalline precipitates,which are white or yellowish in color, with amines in acid solutions. In order to establish the sensitivity of this reaction, we found the limiting dilution at which, after 24 hours, a precipitate appears (Table 1). Precipitation was carried out in 1% acetic acid.

TABLE 1

Limiting Dilution at Which a Precipitate is Formed After 24 Hours

Amine	Dilution	Amine	Dilution
Methylamine	1 : 8400	Aniline	1 : 8300
Ethylamine	1 : 2200	Methylaniline	1 : 25400
Diethylamine	1 : 50000	Dimethylaniline	1 : 8600
n-Butylamine	1 : 15000	Xylidene (1, 3, 4)	1 : 19500
n-Dibutylamine	1 : 200000	Xylidene (1, 4, 5)	1 : 18000
Aminocyclohexane	1 : 200000	Quinoline	1 : 120000
Dicyclohexylamine	1 : 200000	Benzidene	1 : 44000
		Pseudocumene	1 : 8000

Most amines form sparingly soluble precipitates, i.e. they are quantitatively precipitated from weakly acid solutions by sodium tetraphenylboron. Completness of precipitation was checked by the reaction with bindone [10].

---

* I. Barbane and A. Ertnere took part in the experimental section.

On the basis of this preliminary work we attempted to determine amines gravimetrically after their precipitation from weakly acid media with sodium tetraphenylboron. The precipitates settled out rapidly and could be readily filtered. Difficulties arose, however, when we tried to dry the precipitates. We could not get good reproducible results whether we dried them in air or in a vacuum, because we could not get constant weight. In the best cases, we got 90-97% of the theoretical value, but in some individual cases we got results as low as 50%, presumably because of the comparatively high volatility of these compounds. The results obtained cannot be explained by incomplete precipitation, since on testing the evaporated filtrate with bindone, a negative reaction for amine was obtained.

On the basis that precipitation is quantitative, but that part of the precipitate is lost during further treatment, we decided to work out a titrimetric method, and, for this purpose, modified slightly the method proposed by Rudorf and Zannier for determining potassium [8].

The principle of this method is as follows. To the solution containing the amine is added an excess of sodium tetraphenylboron and the mixture diluted to a known volume. After filtering off the precipitate, any $Na[B(C_6H_5)_4]$ remaining in the filtrate is precipitated with silver nitrate. Silver tetraphenylboron is precipitated and then filtered off, and excess silver determined by means of thiocyanate. Removal of amine which might go over into the precipitate is very desirable, since silver tetraphenylboron is less soluble than the amine tetraphenylboron. Accordingly, the latter, in the presence of Ag+ ions will be converted into $Ag[B(C_6H_5)_4]$, which means that too much $AgNO_3$ will be used and that low results will be obtained.

Test solutions should be free of anions which can precipitate with silver ions (Cl^-, Br^-, I^-, CN^-, SCN^-, etc). Determination is carried out in nitric, sulfuric, or acetic acid solutions.

To check on this method we used amines either in the free form or as their salts. All materials were either distilled or recrystallized before use. When hydrochlorides were used, the chloride ion content was determined and allowance made for it in calculations on the amount of $AgNO_3$ used. The boiling or melting points, respectively, of the materials used were in fair agreement with published data (given in brackets below); this served as a criterion of their purity.

n-Butlyamine, B.p. 78° (77.8°)
n-Dibutylamine, B.p. 159° (158°)
Aminocyclohexane, B.p. 132° (134°)
Dicyclohexylamine, B.p. 253° (254°–256°)
Aniline, B.p. 184.5° (184.4°)
Methylaniline, B.p. 195° (196°)
Dimethylaniline, B.p. 192.5° (192.5-193.5°)
Quinoline, B.p. 236° (237.7°)
Xylidene (1, 4, 5), B.p. 212° (213.8°)
Xylidene (1, 3, 4), B.p. 213° (216°)
Pseudocumene (recrystillized from alcohol), M.p. 68° (68°)
m-Toluylenediamine (recrystialized from water), M.p. 99° (99°)
Benzidine (recrystallized from water) M.p. 127° (128°)
Ethylamine hydrochloride, M.p. 108° (108°)
Diethylamine hydrochloride (recrystiallized from absolute alcohol) M.p. 227° (228 - 229°).

Standard solutions were made by weighing out and dissolving known amounts of material in standard flasks.

The sodium tetraphenylboron used should be free from chloride ions, accordingly, we modified slightly the method which has been described previously for preparing the reagent [9]. During the course of the work it became manifest that there is no need to dry under vacuum the sodium tetraphenylboron precipitated by salting out. The precipitate which has been sucked dry on a Buchner is dried at 55-60°, there being no need to remove all the water from it. When the preparation is dry enough to be ground up in a mortar, it is treated in a conical flask with a small amount of ether saturated with water. Cooling in ice water speeds up solution of sodium tetraphenylboron [11]. The ether is sucked off and the operation repeated three times. The ethereal extracts are collected and the ether evaporated off under

TABLE 2

Determination of Amines with Sodium Tetraphenylboron

Amine	Amount taken in mg	Amount found in mg	Error in mg	Error in %
Ethylamine hydrochloride	24.23	24.46	+0.23	0.95
"	24.23	24.50	+0.27	1.10
Diethylamine hydrochloride	27.17	27.44	+0.27	1 00
n-Butylamine	25.72	25.63	−0.09	0.35
"	25.72	25.55	−0.17	0.78
"	25.19	24.90	−0.29	1,15
n-Dibutylamine	25.26	25.34	+0.08	0.32
"	25.26	25.18	−0.08	0.32
"	25.08	24.97	−0.11	0.44
Aminocyclohexane	25.15	25.04	−0.11	0.45
"	25.15	25,06	−0,09	0.36
"	27.93	27.81	−0.12	0.43
"	27.93	27.85	−0.08	0.29
Dicyclohexylamine	25,35	25.23	−0.12	0.51
"	25.35	25.20	−0.15	0.59
Aniline	25.97	25.91	−0.06	0.23
"	25.97	26.06	+0.08	0.31
Methylaniline	64.66	64.24	−0.62	0.65
"	64.66	64.82	+0.16	0.25
Dimethylaniline	31.94	31.99	+0.05	0.16
"	31.94	31.99	+0.05	0.16
Quinoline	32.96	32.75	−0.21	0.64
"	32.96	33.07	+0.11	0.30
Xylidene (1, 4, 5)	31.87	31.72	−0.15	0.47
" (1, 3, 4)	36.02	36.32	+0.30	0,84
" (1, 3, 4)	32.02	31.79	−0.23	0.72
Cumidene	21.59	21.74	+0.15	0,69
m-Toluylenediamine	31.95	31.79	−0.16	0.50
"	31.95	31.67	−0.28	0,84
Benzidine	34.04	33.86	−0.18	0.53

a slight vacuum. The moist precipitate still containing some ether which remains on the bottom of the flask is treated with chloroform. After removal of the chloroform, it is again twice washed with hot chloroform and dried at 60°. In this way a completely white, fine crystalline preparation is obtained which is soluble in water; it contains ~ 97% $Na[B(C_6H_5)_4]$. If, during this procedure, a slight turbidity is obtained, $Al(NO_3)_3$ is added to the solution and the solution then filtered.

Analytical Procedure

Reagents required 1) 0.05 N $AgNO_3$. Standardized with 0.05 N KCl: . 2) ~ 0.05 N NH_4SCN. Standarized with 0.05 N $AgNO_3$; 3) ~ 0.05 N $Na[B(C_6H_5)_4]$. To 10 ml of the solution of $Na[B(C_6H_5)_4]$ in a 100 ml standard flask is added 10 ml 0.05 N $AgNO_3$; the solution is then acidified with acetic acid, diluted to the mark, shaken, and after 10-15 minutes filtered through a dry filter. 20 ml of the filtrate is titrated with ~ 0.05 N NH_4SCN in the presence of ferric alum.

To 5-10 ml of the test solution, in a 100 ml flask acidified with HNO_3, H_2SO_4, or CH_3COOH (pH ~ 3) and containing 15-60 mg of amine, is added 10 ml (a small excess) of 0.05 N $Na[B(C_6H_5)_4]$, water is added to bring the volume up to the mark and then the whole shaken. After 10 minutes the precipitate which has separated out, is filtered through a dry filter. To 50 ml of filtrate in a standard flask is added a small excess of 0.05 N $AgNO_3$, the volume made up to the mark, the whole shaken, and the precipitate of $Ag[B(C_6H_5)_4]$ filtered through a dry filter. Removal of the precipitate is essential to prevent reaction between thiocyanate and silver tetraphenylboron [12]. Excess Ag+ ions are determined in 20 ml of the second filtrate by titration with a solution of ~ 0.05 N NH_4SCN using ferric alum as indicator. Since only an aliquot of the solution is titrated, titration can be repeated several times.

The results obtained in this way are given in Table 2.

Experimental error increases in the case of chlorides (Experiments 1, 2, 3). In all the other cases, the mean error did not exceed 0.50%. There are grounds for believing that sodium tetraphenylboron is a suitable regent for determination of a number of other amines.

The authors wish to thank Prof. G. Vanag for his gift of amines and for valuable advice in carrying out the work.

SUMMARY

1. The sensitivity of the reaction which occurs between sodium tetraphenylboron and some aliphatic and aromatic amines has been determined.

2. A method has been developed for the titrimetric determination of amines with sodium tetraphenylboron.

3. The method of preparing sodium tetraphenylboron has been improved.

LITERATURE CITED

[1] G. Wittig, G. Keicher, A. Rückert, and P. Raff, Ann. 563, 110 (1949); 566, 101 (1950); 573, 195 (195

[2] O.E. Schulz and G. Mayer, Deut. Apoth. Ztg. 21, 358 (1952).

[3] H. Flaschka, A. Holasek and A.M. Amin Arzeneimittel-Forsch. 4, 38 (1954).

[4] R. Fischer, and M.S. Karawia, Mikrochemie ver. Mikrochim. Acta. 4, 366 (1953).

[5] L. Zeidler, Hoppe-Seyler's Z. physiol. Chem. 291, 177 (1952).

[6] G.H. Gloss, Chemist Analyst 42, 50 (1953).

[7] R. Neu, Z. anal. Chem. 143, 254 (1954).

[8] W. Rüdorf and H. Zannier, Z. anal. Chem. 137, 1 (1952).

[9] A.F. Ievinsh and E. Yu. Gudrinietse, J. Anal. Chem. 9, 270 (1954). (T.p. 301).*

[10] G. Wanag, Z. anal. Chem. 113, 21 (1938); 119, 413 (1940); 122, 119 (1941).

[11] A.N. Nesmeyanov and V.A. Sazonova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 1, 187 (T.p. 166).*

[12] M.I. Kolthoff and V.A. Stenger, Volumetric Analysis (Moscow, 1952), Vol II, p. 323.

Received September 28, 1955

---

* T.p. = C.B. Translation pagination.

DETERMINATION OF MONOETHANOLAMINE, DIETHANOLAMINE, AND TRIETHANOLAMINE IN THEIR MIXTURES BY PARTITION CHROMATOGRAPHY

D.A. Vyakhirev and Yu. N. Suloev

Gorky State University

During technical production of ethanolamines there is formed a rather complex mixture containing all three amines, as well as ammonia and carbon dioxide. Analysis of this mixture is carried out at present by fractional distillation under vacuum; this method, however, does not give accurate enough results because of incomplete separation of the mono-, di-, and triethanolamines. In particular it is difficult to distill diethanolamine which has a similar boiling point.

Development of an improved analytical method is highly desirable. To solve this problem we tried to use partition chromatography based on the work of Fuks and Rappoport, who sucessfully used this method for separating a mixture of mono-, di-, and trimethylamines [1].

We used starch as a carrier for the same reasons as those that were outlined in the paper just quoted. Secondary butanol was used as the mobile solvent. Other alcohols which we tested—n-butanol, isobutanol isopropanol, and isoamyl alcohol—proved unsuitable.

~ . 13 g of starch was shaken up with secondary butanol saturated with water. The suspension was poured into a chromatographic column 12 mm in diameter and compressed under a pressure of 150 Hg with compressed air. The height of the starch column was 150 mm. The column thus prepared was used for 10-12 experiments. The number of experiments which can be carried out with the same column presumably can be increased. One factor which prevents a more prolonged use of the same column is the gradual drop in the input velocity of the solvent in the column under constant pressure above the solvent, as a consequence of packing of the starch.

In order to ensure a constant flow rate we used an apparatus consisting of a syringe designed for introducing solvent onto the column, and a mechanism which moves the piston of the syringe at a strictly uniform rate. The construction of this set-up is shown in Fig. 1. The rate at which solvent passes through the column was equal to 0.13 ml/min in all experiments. The volume of solvent which flowed through the column during the experiment was not more than 22 ml. A known volume of the solution of ethanolamines was introduced onto the column, and after it had soaked onto the carrier, the column was connected via a rubber bung to the syringe, and elution carried out. The liquid issuing from the column was collected in a beaker containing distilled water, and titrated with hydrochloric acid, using Methyl Orange as indicator. Before analysis, the test technical mixture was heated on a water bath at 100° for 15-20 minutes to remove any ammonia completely (ammonia interferes with determination of triethanolamine).

Whether or not separation of the components of the mixtures is complete, and what their quantitative compostions are, can be judged from the output titration curves. These curves were constructed by plotting the number of ml of hydrochloric acid used in titration along the ordinate, and the time which has elapsed from the commencement of washing of the column along the abscissa.

In Fig. 2 is shown the curve obtained for 0.2 ml of the technical product which has been heated beforehand on a water bath (for removal of ammonia), and diluted 10 times with secondary butanol saturated with water. As can be seen from the curve, the components issuing from the column follow one another closely. Triethanolamine is first eluted from the column (Step 1), this is followed by diethanolamine (Step 2), while the last to issue is monoethanolamine (Step 3). The height of the step corresponding to the given component is proportional to the content of that component in the sample taken for analysis, while the magnitude of the horizontal parts of the curve testify to completeness of separation. Extension of the horizontal parts of the curve, i.e. improvement in separation, can be achieved by decreasing the amount of material introduced into the column, or by increasing the size of the latter.

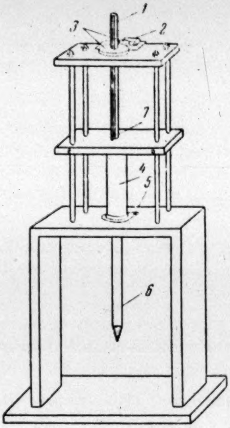


Fig. 1. Apparatus for ensuring a constant flow rate of solvent during chromatographic separation of a mixture of ethanolamines: 1) micrometric screw with slot; 2) Warren motor; 3) cog; 4) "Record" syringe (20 ml); 5) arresting device; 6) chromatographic column; 7) controlling side piece.

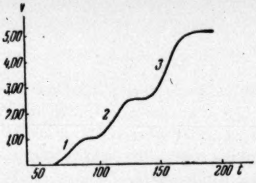


Fig. 2. Output curve for a mixture of triethanolamine, diethanolamine, and monethanolamine. Amount of mixture of ethanolamines 0.2 ml; diluted 10 times with secondary butanol saturated with water; v - volume of 0.05 N HCl in ml; t - time in minutes.

On decreasing the amount of test material further, the accuracy of the method will be determined primarily, not by the performance of the chromatographic column, but by the sensitivity of the eye to changes in color of the indicator during titration.

Results of three experiments on separation and analysis of a production sample of the mixture of ethanolamines are given in the table. Titration was carried out with 0.05 N HCl. In each case 0.2 ml of test liquid diluted ten times was introduced onto the column. As the titration results show, the mean experimental error for determination of triethanolamine amounts to 4.5% of the arithmetic mean of three results; since complete separation of the mixtures was achieved, such a comparatively high error is determined only by inaccuracy of titration, insufficient sensitivity of the eye to indicator color changes.

To increase accuracy and automatize the analysis, it is proposed further to use photocolorimetric titration or to increase the sizes of column and syringe used for feeding solvent onto the column.

TABLE

Chromatographic Separation of a Technical Mixture of Ethanolamines

Experiment number	Monoethanaolamine				Diethanolamine				Triethanolamine			
	Amt. of acid titrated, ml	Concentration of material as determined		Deviation in % from mean value	Amt. of acid titrated, ml	Concentration of material as determined		Deviation in % from mean value	Amt. of acid titrated, ml	Concentration of material as determined		Deviation in % from mean value
		N	in g/l			*N*	in g/l			*N*	in g/l	
1	2.45	6.12	372	−4.6	1.45	3.60	378	+4.4	1.00	2.50	372	+3.3
2	2.60	6.50	396	+1.5	1.40	3.50	368	+1.7	0.90	2.25	335	−6.9
3	2.65	6.62	403	+3.4	1.30	3.25	341	−5.8	1.00	2.50	372	+3.3
Mean arithmetical	—	—	390	3.2	—	—	362	4.0	—	—	360	4.5

SUMMARY

1. Conditions have been established for complete separation of synthetic mixtures of mono-, di-, and triethanolamines by the method of column partition chromatography. The conditions are as follows: carrier – 13 g starch; developing solvent – secondary butanol saturated with water; flow rate of solvent through column – 0.13 ml/minute for a column with internal diameter 1.2 cm; column temperature – 15-18°; optimum amounts of material to be introduced onto the column: mono ethanolamine – 0.0078 g; diethanolamine – 0.0072 g, and triethanolamine 0.0072 g.

2. A method has been developed for chromatographic separation of technical mixtures of ethanolamines. Experimental error for the components is less than 5%; an analysis takes 3 hours.

LITERATURE CITED

[1] I. A. Fuks and M. A. Rappoport, Proc. Acad. Sci. USSR 60, 1219 (1948).

Received May 26, 1955

BLANK
PAGE

PHOTOCOLORIMETRIC MICRO METHOD OF DETERMINING LACTOSE AND SACCHAROSE WHEN THEY ARE PRESENT TOGETHER IV.

M. N. Tulchinsky

Leningrad Technological Institute of the Refrigerator Industry

In a previous publication it was shown that different reducing sugars in equimolecular concentrations, under the same reaction conditions, exhibit different reducing capacities with respect to potassium chromate in the presence of sodium carbonate [1].

Reduction of trivalent chromium to hexavalent chromium by sugars, in the presence of sodium carbonate or potassium carbonate, leads to the formation of a complex compound of trivalent chromium which has a green color. The increase in intensity of the green color of the solution on increasing the amount of sugar in solution was used for developing a photocolorimetric method of determining small amounts of lactose [2], and as a quantitative characteristic for lactose hydrolysis [3].

Results are given in the present article relating to the development of a photocolorimetric method of determining the amounts of lactose and saccharose when they are simultaneously present, on the basis of the difference in behavior of saccharose and lactose towards potassium chromate in the presence of sodium carbonate.

EXPERIMENTAL

Saccharose, in contrast to lactose, does not reduce potassium chromate in alkaline media. Accordingly, if both lactose and saccharose are present together in solution, then it should be possible to determine lactose directly [2], while the amount of saccharose can be determined after hydrolysis, on the basis of the reducing capacity of the saccharose hydrolyzate.

For our investigations we used lactose monohydrate which had an m.p. of 203°, and saccharose having an m.p. of 184°. The latter was hydrolyzed [4]. The effect of sugar concentration on the intensity of the color formed during interaction of the sugars with oxidizing solution was studied for the saccharose hydrolyzate obtained from various amounts of saccharose (from 0.5 to 3.0 mg) against a background of a lactose solution containing from 0.5 to 2.0 mg of the latter. Reaction between sugars and oxidizing solution containing 6 ml of 0.25 N K_2CrO_4, 3 ml of 2N Na_2CO_3 and 1 ml of 40% glycerol solution was carried out by heating the reaction mixture (total volume 12 ml) in test tubes in a boiling water bath in the course of 15 minutes. The control which consisted of oxidizing solution and water was heated under the same condition.

When there is less than 2 mg of reducing sugars in the indicated volume of reaction mixture, a turbidity develops which interferes with measurement of the color of the solution. In order to get transparent solutions, therefore, we used glycerol(which has been used before for getting a soluble copper-glycerol complex, during subsitution of Rochelle salt by glycerol [5]) in Bertrand's method of determining sugars.

The intensity of the color formed during interaction of sugars and oxidizing solution was measured on a FEK-3 photocolorimeter fitted with a yellow filter (maximum transmission at 550-600 mμ). The results obtained are shown in the curves on Fig. 1.

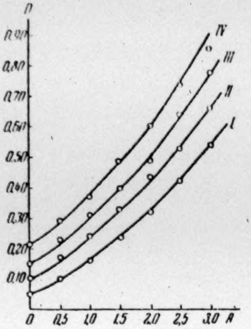


Fig. 1. Relation between color intensity of the reaction mixture and concentration of lactose and saccharose: D) optical density; A) amount in mg of saccharose taken for hydrolysis. Supporting solution of lactose: I) 0.5 mg; II) 1.0 mg; III) 1.5 mg; IV) 2.0 mg.

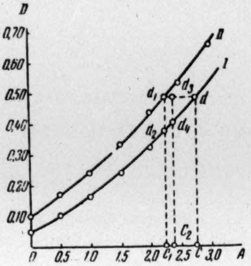


Fig. 2. Calculation of the amount of saccharose in a supporting solution of lactose: D) Optical density; A) amount in mg of saccharose taken for hydrolysis. Lactose supporting solution: I) 0.5 mg; II) 1.0 mg.

It is clear from these results that the color intensity of the reaction mixture, as a function of the concentration of saccharose hydrolyzate, does not obey Beer's law. Subsequent experiments were carried out to establish the possibility of determining saccharose in milk in the presence of lactose. The lactose source was the same amount of milk in each case, while the saccharose was added in varying amounts to the milk. To each of five 100 ml standard flasks was added 2 ml of milk and the following amounts of saccharose: 100, 150, 200, 250, and 300 mg, and followed by 25 ml of water in each case. After precipitation of the milk proteins, and addition of water to each flask to bring the volume up to the mark, clear solutions were obtained on filtration, containing in 1 ml the lactose from 0.02 ml of milk, and following corresponding amounts of saccharose: 1.0, 1.5, 2.0, 2.5, and 3.0 mg. For saccharose determination, 25 ml of filtrate was hydrolyzed in a 50 ml flask.

The lactose was determined by taking 1 ml of filtrate before hydrolysis, while for saccharose determination, in the same supporting solution of lactose, 2 ml of the saccharose hydrolyzate was taken from each flask, oxidizing solution added, and the whole heated as indicated above. Solutions were obtained possessing different color intensities, formed under the influence of the lactose from 0.02 ml of milk and saccharose hydrolyzates from 0.0, 1.0, 1.5, 2.0, 2.5 and 3.0 mg saccharose. The results obtained are given in Table 1.

On the basis of the results given in Table 1 and the calibration curves in Fig. 1 which express the relation between optical density of the reaction mixture and saccharose concentration (saccharose hydrolyzate) in supporting solutions of 0.5 mg and 1.0 mg, respectively, of lactose, the amount of saccharose in a supporting solution of milk lactose was calculated (Table 2).

TABLE 1

Color Intensity of the Reaction Mixture, Formed Under the Influence of Milk Lactose and Milk Lactose + Saccharose Hydrolyzate

	Lactose background from 0.02 ml of milk					
Amount in mg of saccharose taken for hydrolysis	0.0	1.0	1.5	2.0	2.5	3.0
D (optical density)	0.09	0.22	0.30	0.41	0.49	0.60

TABLE 2

Determination of Saccharose in a Supporting Solution of Milk Lactose (0.9 mg of lactose from 0.02 ml of milk)

Saccharose taken in mg	1.00	1.50	2.00	2.50	3.00
Saccharose found in mg	0.95	1.45	1.95	2.40	2.85

The deviation between the amount of saccharose taken and that actually found is within the permissible limits of error for photocolorimetric methods of analysis [6]. The amount of sugar which can be determined by the given method brings this method into the category of micro methods [7].

Analytical Procedure

Calibration curves expressing the relation between the intensity of the color of reaction mixture, which develops on heating the oxidizing solution with sugars, and the amount of sugars in the saccharose hydolyzates obtained from 1.0, 1.5, 2.0, 2.5, and 3.0 mg of saccharose in a supporting solution of 0.5, 1.0, 1.5, and 2.0 mg lactose, were first constructed. For this purpose standard solutions of lactose and saccharose were prepared. The standard solution contains 1 mg of lactose in 0.5 ml of solution (0.1053 g of lactose monohydrate in 50 ml solution).

In order to prepare a standard solution, 0.1250 g of saccharose was dissolved in 25 ml of water in a 50 ml flask and hydrolysis carried out in the presence of 2.5 ml hydrochloric acid (120 ml concentrated HCl, diluted with water to 200 ml) by heating in a water bath at a solution temperature of 67-70° for 10 minutes.

The solution was cooled and neutralized with 0.75 g Na_2CO_3 (weak acid reaction); 0.4 ml of the saccharose hydrolyzate obtained corresponds to 1 mg of saccharose. Into 15-16 ml test tubes of the same diameter and wall thickness was introduced the oxidizing solution (6 ml of 0.25 N K_2CrO_4 solution, 3 ml of 2N Na_2CO_3 solution, and 1 ml of 40% glycerol), and various amounts of solutions of the sugars and sufficient water so that the total volume of the reaction mixture was 12 ml. Control solutions consisting of 10 ml oxidizing solution and 2 ml water were prepared in two test tubes. Reaction mixtures and control solutions were mixed, all of them stoppered with corks through which passed a glass tube 20 cm long which acted as air-cooled condenser; each was heated in a boiling water bath for 15 minutes, taking care that the level of the water in the bath was higher than the level of the reaction mixtures in the test tubes. The solutions were cooled to room temperature in running water and then measured photocolorimetrically, using the control solutions as blanks; calibration curves are drawn on the basis of the results. Colors of standard solutions, with respect to optical density, can be imitated by colored solutions of mineral salts.

For determination of sugars in milk products, protein was precipitated in order to get transparent and colorless solutions. 2 ml of milk or milk product diluted appropriately (the sugar contents of this should lie within the limits of the calibration curves) was introduced into a 100 ml standard flask; this was followed by 25 ml water, and 2 ml of a 10% solution of $Al_2(SO_4)_3 \cdot 18H_2O$, 2 ml of 0.45 N NaOH, and 2 ml of saturated NaF solution for precipitating protein. The contents of the flask were mixed and left for 15 minutes. Water was added to bring the volume up to the mark, the whole mixed and then filtered twice through the same smooth filter.

Saccharose hydrolyzate was prepared by hydrolyzing 25 ml of the filtrate in a 50 ml flask; the solution was then neutralized to a weak acid reaction and water added to bring the volume up to the mark. For determination of the amount of lactose 1 ml of filtrate before hydrolysis was taken and 1 ml of water, and 10 ml of oxidizing solution added; while for determining the saccharose content in the same supporting concentration of lactose, 2 ml of filtrate after hydrolysis was taken, 10 ml of oxidizing solution added, and the whole heated as indicated above; the mixture was then cooled and its color measured with respect to control solutions; the amounts of lactose and saccharose were finally determined from the calibration curves.

The amounts of lactose and saccharose, respectively, are calculated as follows. E.g., from Table 1 the optical density of a solution after interaction of filtrate before hydrolysis (milk lactose) with oxidizing solution is equal to 0.09, while for a solution of saccharose hydrolyzate, in the same supporting solution of lactose, it is equal to 0.49 (2.5 mg saccharose). By means of the calibration curve on Fig. 1 the amount of lactose is determined

$$\begin{array}{r} 1.0\,\text{mg} - 0.10 \\ c_x - 0.09 \end{array} \qquad c_x = \frac{1.0 \cdot 0.09}{0.10} = 0.9\,\text{mg}$$

Since the amount of lactose is equal to 0.9 mg, then for determining the amount of saccharose in a supporting solution containing 0.9 mg lactose, one makes use of the two calibration curves for saccharose **hydrolyzates** in supporting solutions of lactose containing 0.5 and 1.0 mg **respectively**. These calibration curves of Fig. 1 which are necessary for calculation are shown in Fig. 2.

It can be seen from Fig. 2 that if the saccharose hydrolyzate leads to development of a color with an optical density of 0.49 in a supporting solution of 0.5 mg lactose, then the saccharose concentration can be determined by dropping a perpendicular from point d onto the abscissa, i.e., saccharose concentration would be equal to c. In exactly the same way it is possible to calculate that for a concentration of the supporting solution of 1.0 mg, and an optical density of 0.49, the saccharose concentration would be c_1.

For one and the same optical density (in the given instance 0.49) and on shifting from d to d_1, there is an increase in the concentration of the supporting lactose from 0.5 to 1.0 mg, while at the same time the concentration of saccharose decreases. Accordingly, the amount of saccharose in a supporting solution of lactose containing from 0.5 to 1.0 mg lactose, for an optical density of 0.49, will correspond to a point lying between c and c_1. For a saccharose concentration of c_1 in 0.5 mg lactose (from 0.5 to 1.0 mg) the optical density will be $d_2 d_1$. From the graph it is found that $d_2 d_1 = 0.11$. Then for 0.5 mg lactose the optical density is 0.11, while for 0.4 mg lactose (for a lactose supporting solution of 0.9 mg, it is necessary to add 0.4 mg to the 0.5 mg) one calculates by proportion:

$$\begin{array}{l} 0.5\,\text{mg} - 0{,}11 \\ 0.4\,\text{mg} - D_x \end{array} \qquad D_x = \frac{0.4 \cdot 0.11}{0.5} = 0.09.$$

Next, a point is found on $d_1 d$ which is separated from $d_2 d$ by 0.09 on the optical desity scale. Such a point will be d_3, while $d_3 d_4$ will correspond to an optical density of 0.09 for 0.4 mg of lactose (from 0.5 to 1.0 mg) or d_3 will correspond to a supporting solution of lactose containing 0.9 mg (from 0.0 to 1.0 mg).

By dropping a perpendicular from d_3 onto the abscissa one gets c_2 which corresponds to 2.40 mg of saccharose in a supporting solution containing 0.9 mg of lactose.

SUMMARY

1. A photocolorimetric micro method has been developed for quantitative determination of lactose and saccharose when they are both present simultaneously; it is based on reduction of potassium chromate by lactose and saccharose hydrolyzate, in the presence of sodium carbonate and glycerol.

2. The amount of saccharose in the presence of lactose is calculated graphically on the basis of the results of the optical density of a solution of lactose and that of a solution of lactose + saccharose hydrolyzate, using calibration curves which express the relation between optical density of the solution and saccharose concentration (saccharose hydrolyzate) in two supporting solutions of lactose of different concentrations.

3. There is reason to believe that it may be possible to use this method for determination of saccharose in the presence of other reducing sugars apart from lactose.

LITERATURE CITED

[1] M.N. Tulchinsky, J. Appl Chem. (USSR) 23, 2, 176 (1950) (T.p. 181).*

[2] M.N. Tulchinsky, J. Appl. Chem.(USSR) 24, 2, 179 (1951) (T.p. 193).*

[3] M.N. Tulchinsky, J. Appl. Chem.(USSR) 26, 2, 204 (1953) (T.p. 175).*

[4] G.S. Innikhov, Analysis of Milk, Milk Products, and Materials of the Milk Industry (1930), p. 202.

[5] M.N. Tulchinsky, J. Appl. Chem. (USSR) 11, 4, 707 (1938).

[6] A.K. Babko and A.T. Pilipenko, Colorimetric Analysis (1954), p. 12.

[7] I.M. Korenman, Quantitative Microchemical Analysis (1949), p. 9.

Received May 25, 1955

---

* T.p. = C.B. Translation pagination.

BLANK
PAGE

BRIEF COMMUNICATIONS

METHODS FOR THE ISOTOPIC ANALYSIS OF WATER

1. A NEW APPARATUS FOR THE FALLING-DROP METHOD OF ISOTOPIC ANALYSIS OF WATER

A.I. Shatenshtein and Ya. M. Varshavsky

The L. Ya. Karpov Physicochemical Institute, Moscow

The falling drop method of isotopic analysis of water is convenient in the sense that only a small amount of water (less than 0.1 ml) is necessary, and measurement can be carried out in a matter of minutes. At constant temperature there is a change in the dropping time of a water drop of standard size, through a fixed layer of a liquid of suitable density and viscosity which is immiscible with water. The fall of a water drop through a liquid medium does not obey Stokes' law quantitatively. Accordingly, in order to determine the density of water (and its deuterium concentration) from the time of fall of a drop, use is made of a calibration curve which has been prepared beforehand (for literature on the falling-lrop method see [1].

A number of droppers have been described in the literature for obtaining water drops of standard size [1]. Nevertheless, even the best of them is large and inconvenient to use [2]. The amount of mercury required to fill them is large. This leads to the danger of formation of air bubbles, and to appreciable variations in the volume of mercury with room temperature changes. Another drawback is the necessity of using a vacuum for dropper with mercury.

A dropper is described below which is free from these drawbacks. Several liquids have been suggested for the drop method in the literature. The use of individual materials – ortho- and metafluorotoluene [3] – is convenient. By means of these liquids, at constant temperature it is possible to carry out measurements in the range 0 to 3 at.% D, while by changing the temperature (not very convenient in practice) the concentration range of D can be extended to 6 at.%. These liquids, however, are not readily available. A mixture of methylsalicylate and mineral oil is too viscous [4]. A solution of phenanthrene in α-methylnaphthalene is suitable only for analysis of water with a D concentration from 10 to 40 at.%. The vapor pressures of bromobenzene and xylene, the mixture of which has been the one most often used [5], differ appreciably. This difference is smaller if, instead of bromobenzene, chlorobenzene is used, as we have done in the given instance.

The dropper (Fig.1) is fixed in a stand (17), 20-25 cm long, at the base of which (19) there is a groove 40 mm wide. It can be moved up or down by means of a sleeve (12) fitted with a screw (13). Into the body of the dropper (diameter 15 mm, length 40 mm) equipped at the top with a screw (2) (diameter 6 mm, pitch 0.5 mm) and with a head (1); into the lower end of the body is screwed a bushing (6), into which, with the help of a low melting alloy (e.g. Wood metal), is fitted a glass capillary (7). The over-all length of the capillary is 100 mm. Its upper end has an internal diameter 3 mm, while the middle part is 1.2-1.3 mm; the lower end, which is drawn out, is cut off evenly and has a diameter of 0.2-0.3 mm.

Screw (2) rests on the head of a piston (4) ground down to fit into the widened part of the capillary.

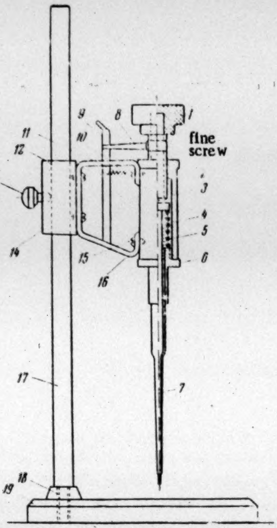


Fig. 1

Between the head of the piston and the bushing there is a stiff steel spring (5), which is compressed when, on screwing in the screw, the latter is pressed on to the piston. on unscrewing, the spring is compressed and the piston lifts upwards.

The capillary is filled with mercury, the level of which is changed according to the position of the piston. For one turn of the screw the piston forces out a drop with a volume of 3.5 mm³ .

The screw is provided with a stop pin (8), which allows one to fix each turn. During rotation of the screw it pushes against the locator (9) which is fitted onto the frame (16), which fixes the body of the micro-dropper to the stand. On drawing out the locator to its extreme position, permitted by the groove in the frame, the stop pin of the screw does not hold, and the screw can be freely rotated.

The stopper is assembled as follows. First the glass capillary is fixed in the bushing. To do this, the capillary is placed in the bushing and the gap between glass and metal filled up with Wood's metal. After the alloy has set, its surface is covered with a layer of a low-melting lubricant (e.g. picene) so as to prevent any mercury leakage. The capillary is then filled (through the wide end) with mercury so that not a bubble of air remains, and the piston covered with thick vacuum grease, with the spring already fitted on it, placed in it. Excess mercury is squeezed out of the capillary. The bushing and capillary are screwed into the body and some mercury squeezed out.

The glass test tube shown in Fig. 2, on which have been marked two circular rings at distances of 50 and 250 mm from the bottom, is filled with a mixture of xylene and chlorobenzene, the density of which (d_4^{20}) is equal to 0.996. The final composition of the mixture was fixed so that the dropping time of distilled water lay within the limits of 70-80 seconds. A selection of mixtures with varying amounts of xylene and chlorobenzene, in principle, allows one to determine the density of heavy water containing any amount of deuterium. In such cases, dropping time of the very lightest test sample in the given interval should to 70-80 seconds. Nevertheless, in practice it is most convenient to use a mixture of xylene and chlorobenzene which can be used covering the range 0 to 5 at % of deuterium.

During measurements, test tube and mixture are immersed in a thermostat (25 ± 0.003°), which has a narrow vertical window. After the tube and mixture have been fixed vertically (by means of a plumb line), the capillary of the dropper is washed with the test. To do this, the tip of the capillary is immersed to 2-3 mm in water, which is drawn up by turning the screw 5-6 times. The dropper is then lifted on the stand, and, by turning the screw, the liquid is squeezed out onto thick non-porous paper. The stand plus dropper are placed on the top of the thermostat so that the opening of the tube containing the mixture is underneath the capillary. Test water is taken into the capillary and the dropper is let down so that the capillary tip is immersed to 2-3 mm in the mixture. The screw is turned through one revolution until the stop pin presses up against the locator. When this is done, a drop of water is formed on the capillary tip. Dropper and stand are lifted up carefully so that the water drop is cut off by the surface layer of the mixture. A stopwatch is used to measure the time for 3-4 drops to pass between the first and second marks (with an accuracy of 0.1-0.2 seconds). It is desirable that the dropping time be measured more than once, taking in a new lot of water for the repeat. After determination of the mean dropping time, deuterium concentration is determined from the calibration curve.

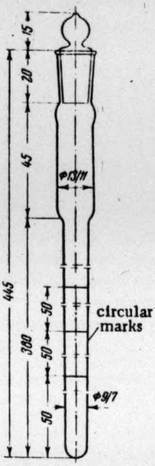


Fig. 2

The calibration curve is constructed by determining dropping time (t) of 8-10 water samples with known deuterium concentrations. The curve is plotted on millimeter scale paper (50 × 50 cm) with 1/t along one axis and deuterium concentration along the other. The curve thus plotted is not far from a straight line. On the basis of the curve obtained it is possible to compile a table of deuterium content of water and the corresponding length of dropping times (in 0.2 second intervals). Such a table is much more convenient to use than a graph and is more reliable. The calibration curve (or table) can only be used under conditions where dropping time is determined by means of the same dropper, test tube, mixture, and where the temperature is identical to the used for constructing the calibration curve. Before carrying out any measurements the dropping time of distilled water is checked.

The accuracy of a determination of D concentration on the first part of the calibration curve (covering the range 0 to 6% deuterium) is 0.02 at.% (two units in the fifth place of the density), while towards the end of the curve, it is 0.05 at.%.

It should be borne in mind that the drop method of isotopic analysis of water, just like other densimetric methods, gives the total deuterium plus heavy oxygen isotopes content. Accordingly, in order to determine the deuterium content of tests which are rich in the heavy isotopes of oxygen, the concentration of the latter should be determined independently.

The technique described in this article for isotopic analysis of heavy water has been in use in our laboratory from 1947 and has completely justified itself.

We should like to thank E. Ya. Alksnisa for help in constructing the dropper, and O.P. Gei for helping in checking the method and carrying out hundreds of measurements.

SUMMARY

A simple and convenient construction of a dropper for the drop method of isotopic analysis of water is described; a suitable liquid is also described.

LITERATURE CITED

[1] M. Kon, Determination of Deuterium by the Falling-Drop Method: Symposium on Production and Determination of Labeled Atoms (Foreign Lit. Press, 1948); I. Kirshenbaum, Heavy Water (Foreign Lit. Press, 1953), p. 330.

[2] F. Rosebury and van Heyningen, Ind. Eng. Chem., Anal. Ed. 14, 363 (1942).

[3] A. Keston, D. Rittenberg and R.Y. Shoenheimer, J. Biol. Chem. 122, 227 (1937).

[4] B. Kahan, Clin.J. Invest. 17, 1158 (1938).

[5] H. Barbour and W. Hamilton, J. Biol. Chem. 69, 625 (1926).

Received June 21, 1956

BLANK
PAGE

IODOMETRIC DETERMINATION OF IODIDES

B.I. Leonov

Kishinev Medical Institute

In acid media, in the presence of excess oxidizing agent, it is impossible to titrate the iodine which separates out during oxidation of iodide because of oxidation of iodide formed during the titration. Accordingly, in the iodometric determination of iodides, one must resort to oxidization of iodide to iodate [1], use of nitrite as oxidizing agent, with subsequent removal by urea [2], etc. Since presence of acid favors oxidation of the iodide formed, we thought of neutralizing the acid before titration with thiosulfate, after which all the iodide will be oxidized.

Since an alkali medium was out of the question in this case, we tried addition of excess dry barium carbonate. When this is done chromate is precipitated simultaneously.

On the basis of the experiments we carried out, the following method of determining iodides was worked out: to 5-25 ml of test solution containing from 50 to 300 mg of iodide in a conical flask is added 5 ml of 1 N $K_2Cr_2O_7$, 10 ml of 4N HNO_3, or 4N HCl and the whole left to stand for 5-10 minutes. For preventing loss of iodine by volatilization it is best to cool the flask under a tap before neutralization. 6 g of barium carbonate is then added and time given for effervescence to cease after shaking. 5 ml of 1 N KI is next added and the mixture titrated with sodium thiosulfate, shaking all the time (starch is added as usual toward the end point), till the greyish blue color disappears. Calculation is made as usual.

In order to establish the advantages and drawbacks of the technique just described, we compared it with a number of other methods in use for determining iodides.

During determination of iodide by oxidation to iodate by means of bromine vapor, according to V.I. Petrashen's method [1] (this method is recommended for analysis of cooking salt), it turned out that when working with decinormal solutions, it is practically impossible to get a correct idea of how much bromine vapor to add. Accordingly for comparison, we chose 1) a method of oxidizing iodide to iodine by means of sodium nitrite, using urea for destroying excess nitrite, according to I.M. Kolthoff's method [2]; 2) titration of iodide with potassium iodate with addition of chlorofrom according to I.M. Korenman's method [3].

Test solutions were prepared by dissolving the exact amount of special grade (chemically pure GOST* 4232-48) potassium iodide. The calculated amount of iodine was taken as being correct. Potassium iodate and potassium dichromate were chemically pure and analytical grades, respectively, while barium carbonate was pure grade. The barium carbonate was checked for absence of any effect on titration of iodine with thiosulate.

Table 1 contains the results of ten replicate determinations of equal amounts of iodide by each of the methods being compared.

By reproducibility is to be understood the difference between the highest and lowest result from a series of equal determinations, expressed as a percentage of the determined amount.

From Table 1 it is clear that the reproducibility of determinations by the technique developed is appreciably higher than in the other methods compared with it.

---

* All Union State Standard - Publisher's note.

Table 2 contains results for determination of different amounts of iodide by the method developed and by the $NaNO_2$

Mathematical treatment of the results obtained by mathematical statistics as outlined in the work of E. G. Grachev [4], and N.P. Komar [5], helped to find two "obviously incompatible" results—0.2646 in line 8, Table 1, and 0.0659 in line 1, Table 2, which shows that in carrying out determinations by means of the nitrite method, a systematic error may crop up. These results were left out.

For each method, the probable error was calculated as well as the mean square error for the case where differerent amounts of iodide were determined. The results obtained show that the method developed has some advantages if the work is carried out with solutions of suitable concentration. In very dilute solutions, and particularly where the acidity is too low, low results may be obtained.

Chlorides have very little effect. A hundred fold excess of chloride increases the result only by 2% of t actual amount.

Bromides exert a stronger effect. The same amount of bromide as iodide leads to an increase of 2%.

TABLE 1

	By the $BaCO_3$ varient	By the $NaNO_2$ method	By the $CHCl_3$ method
I^- taken in g	0.2544	0.2544	0.1273
I^- found in g	0.2553	0.2559	0.1338
	0.2552	0.2544	0.1273
	0.2547	0.2551	0.1325
	0.2551	0.2560	0.1312
	0.2545	0.2544	0.1338
	0.2542	0.2563	0.1351
	0.2542	*0.2646*	0.1286
	0.2535	0.2549	0.1286
	0.2545	0.2551	0.1299
	0.2548	0.2559	0.1273
Amount found at a confidence level of 0.99	0.2546 ±0.0006	0.2552 ±0.0014	0.1308 ±0.0047
Reproducibility, %	0.71	4.01	6.13
Probable error, %	0.24	0.55	3.59

TABLE 2

Experiment number	By the $BaCO_3$ variant		By the $NaNO_2$ variant	
	I^- taken in g	Found	I^- taken in g	Found
1	0.0636	0.0637	0.0636	0.0659
2	0.1273	0.1269	0.1273	0.1273
3	0.1908	0.1910	0.1908	0.1898
4	0.2544	0.2537	0.2544	0.2552
5	0.3178	0.3170	0,3178	0.3173
Mean square error	0.0023		0.0035	
Probable error (in %) at a confidence level of 0.99	0.5		1.05	

From what has been said it follows that the method developed, from an analytical point of view, has some advantages, and can be successfully used for determination of iodides in solutions containing 10 mg of iodine in 1 ml, and more.

SUMMARY

A method has been worked out for iodometric determination of iodides by oxidizing them to free iodine in acid media, with subsequent removal of excess acid and dichromate with dry barium carbonate before titration of iodine with thiosulfate.

This method has been compared experimentally with methods involving nitrite for oxidation and subsequent memoval of excess nitrite with urea, and titration with iodate in the presence of chloroform.

Mathematical treatment of the results showed that the method developed has its advantages.

LITERATURE CITED

[1] V.I. Petrashen, Volumetric Analysis (State Chem. Press, 1949), p. 266.

[2] I.M. Kolthoff and E.B. Sendel, Quantitative Analysis (State Chem. Press, 1948), 651.

[3] I.M. Korenman, Quantitative Microchemical Analysis (State Chem. Press, 1949), 211.

[4] E.G. Gracheva, J. Anal. Chem 7, 48 (1952) (T.p. 51).*

[5] I.P. Komar, J. Anal. Chem. 7, 325 (1952) (T.p. 361).*

Received February 2, 1956

---

* T.p. = C.B. Translation pagination.

BLANK
PAGE

A BISMUTHATE METHOD FOR DETERMINING CHROMIUM IN STEELS NOT CONTAINING VANADIUM

P.F. Agafonov
Metallurgical Factory, Zlatoust

In the present article conditions are described for quantitative oxidation of chromium by sodium bismuthate; a simple method has been worked out for rapid determination of chromium in steels.

In sulfuric or nitric acid media, sodium bismuthate oxidizes trivalent chromium to the hexavalent state

$$2Cr_2(SO_4)_3 + 6NaBiO_3 + 6H_2SO_4 \rightarrow 2H_2Cr_2O_7 + 3Na_2SO_4 + 3Bi_2(SO_4)_3 + 4H_2O.$$

We oxidized chromium in sulfuric acid media, while excess bismuthate was reduced directly in solution with potassium (sodium) chloride.

It was found that quantitative oxidation of chromium depends primarily on solution acidity, temperature, and also the amounts of bismuth and chromium concentration. Complete oxidation of chromium by bismuthate proceeds in the presence of 1-25 ml concentrated sulfuric acid in 100 ml solution.

The most favorable concentration of sulfuric acid is 10-15 ml of the latter in 100 ml of solution.

In contrast to manganese [1, 2], chromium is quantitatively oxidized by bismuthate only when the solution is boiled. Under such conditions the following optimum amounts of sodium bismuthate are necessary: up to 3% Cr (for a steel weight of 1 g) from 1.5 to 2 g; from 3-8% Cr (for a steel weight of 0.2 g from 2 to 2.5 g; from 8 to 25% Cr (for a steel weight of 0.2 g from 2.5 to 3 g; and from 25 to 45% Cr (for a steel weight of 0.2 g) from 3 to 3.5 g of bismuthate.

If insufficient bismuthate is present, incomplete oxidation of chromium occurs, while if excess bismuthate is used, a considerable amount of BiOCl precipitate is formed as a result of hydrolysis; low results are thereupon obtained.

EXPERIMENTAL

An aliquot of high chromium steel (0.2 - 0.5 g)* is dissolved in 20 ml of a mixture of acids (10 ml each of concentrated nitric and hydrochloric acids) in a 500 ml flask. When solution is complete 15 ml of concentrated sulfuric acid is added and the solution evaporated to white fumes of sulfuric acid and initial separation of small amounts of salts. The solution is cooled, 100 ml of hot water added and the salts dissolved by boiling; to the hot solution is then carefully added the respective amount of finely ground sodium bismuthate. The solution is shaken and boiled for 2 minutes. On removal of the flask from the bath, 50 ml of hot water is added, followed by 15-20 ml of 20% potassium chloride (or the same amount of 15% sodium chloride solution), the whole shaken and then boiled for 2 minutes. The solution is cooled, 5 ml of concentrated phosphoric acid is added and chromium titrated with 0.06 N ferrous salt, initially without an indicator until the solution has a weak yellow color; subsequently, 10 drops of indicator is added (0.2% solution of phenylanthranilic acid) and titration continued with ferrous salt until the red-violet color of the solution disappears.

---

* For chromium contents of 3 to 8% in the steel, 0.5 g of the latter is taken, while for chromium contents of 8 to 45%, the amount of sample is 0.2 g.

If the steel contains vanadium (not more than 1%), back titration is used (excess ferrous salt is titrated with potassium permanganate). In order to avoid reduction of permanganate by chloride ions, the permanganate should be added dropwise.

For low chromium steels (containing not more than 3% chromium) 1 g of steel is taken, dissolved in 50-60 ml of sulfuric acid 1 : 3, the solution evaporated to white fumes of sulfuric acid, 100 ml water added, and then the procedure outlined above followed.

If the steel contains large amounts of silicon (greater than 0.80%), then after dissolving the test sample, 5 ml of 4% sodium fluoride solution is added.

Results which illustrate the accuracy of the method are given in the table.

TABLE

Actual Cr content in %	Cr found, in %	Error	Actual Cr content in %	Cr found, in %	Error
0.11	0.11	±0.00	17.58	17.60	+0.02
0.80	0.81	+0.01	21.09	21.17	+0.08
1.14	1.12	−0.02	18.17	18.14	−0.03
1.52	1.52	±0.00	14.64	14.60	−0.04
1.77	1.77	±0.00	32.00	31.90	−0.10

LITERATURE CITED

[1] G. Lendel, D. Hoffman and G. Bright, Analysis of Ferrous Metals (1934).

[2] A. M. Dymov, Technical Analysis of Ores and Metals (Metallurgical Press, Moscow, 1949).

Received September 19, 1955

A NEW COLOR REACTION FOR DIVALENT COBALT

G.D. Nessonova and E.K. Pogosyants*

Moscow Textile Institute

When a solution of cobalt salt is mixed with glycerol and a concentrated alkali solution is subsequently added, a compound is formed which gives the solution an intense blue-violet color. The compound is stable to heat (boiling) and light. On long contact of the solution with air, the blue-violet color gradually changes to green (oxidation of Co^{2+} to Co^{3+}). Addition of a solution of cobalt salt to a mixture of alkali and glycerol, or of glycerol to a mixture of cobalt salt and alkali, does not lead to formation of a blue-violet solution. In both cases the usual blue gelatinous precipitate of cobalt hydroxide [1, 2], is formed.

Complex compounds formed between cobalt and glycerol, which have been described in the literature, and called glycerinates by Grun and Bockish [3], have a red color. It is known that the change in color of the coblat complexes can be related to change in coordination number. In complexes which have a rose or red color, cobalt has a coordination number of six, while blue complexes of this metal have a coordination number of three or four. In blue-colored complexes cobalt is in the form of an anion [4, 5, 6].

Determination of the sign of the charge on the blue-violet compound we obtained confirms what has been said above. During electrolysis of a solution in a U-tube, the boundary of the colored layer invariably moves to the anode. On the basis of published results and our experiments, it can be supposed that the cobalt compound formed with a blue-violet color is a complex compound:

$$Na_{n-2}\,[Co\,(C_3H_8O_3)_{n-m}\,(OH)_m].$$

To detect cobalt, 1 ml of 0.5 N test solution is mixed with 2 ml of glycerol (sp. gr. 1.46) and 1 ml 10 N NaOH added. If cobalt is present the solution immediately acquires an intense blue-violet color; at low cobalt concentrations the color is pale blue. The limit of identification is 0.16 mg/ml Co, limiting dilution 1 : 25, 000.

A spot technique can be used: one drop of test solution of cobalt salt is mixed a porcelain plate with 2 drops of glycerol, and then 1 drop of 10 N NaOH added. A bright blue spot appears.

The color reaction described can be used successfully for qualitative detection, and also for the colorimetric determination of cobalt.

LITERATURE CITED

[1] F.M. Perelman, A. Ya. Zovorykin and N.V. Gudima, Cobalt (Acad. Sci. USSR Press, 1949).

[2] A. Grün and F. Böckisch, Ber. 41, 3465 (1908).

---

* The following students took part in the work: M. Ginsburg, G. Ivanova, A. Dominetskaya, and V. Pron.

[3] G.S. Goldberg, Candidate's Thesis (1946).

[4] L. Katzin and E. Gebert, J. Am. Chem. Soc. 75, 2830 (1953).

[5] H. Denhama, Z. physik. Chem. 65, 641 (1909).

[6] V.P. Zhivopistsev, Candidate's Thesis (Molotov, 1951).

[7] E. Nichol, Can. J. Chem. 31, 145 (1953).

Received May 8, 1955.

A HIGHLY SENSITIVE REACTION FOR HYDROGEN PEROXIDE

I.L. Roikh

Odessa Technological Institute

Photographic plates are freed from silver bromide by treating them with thiosulfate solution: subsequently they are immersed for 2-3 minutes in a mixture of equal volumes of 0.8% $K_4Fe(CN)_6$ solution and 0.4% $FeCl_3$ solution. After soaking, the plates are withdrawn and allowed to dry. For detecting hydrogen peroxide it is desirable that the soaked plates be used soon after preparation, approximately within 24 hours.

If a plate which has been treated in this way is placed in an aqueous solution of hydrogen peroxide, then in the respective places there will appear a blue color which is more intense than that of the background. This enhanced blue color itself disappears in 6-7 days.

Using colored plates it was established that during atmospheric corrosion of metals hydrogen peroxide is formed. On placing magnesium plates protected by emery cloth at a certain angle with respect to a colored plate, so that a wedge formed by the air is obtained, then after 10 minutes, when cleaning is carried out each minute, there is observed a fall in density of the color with increasing distance from the metal surface. An increase in density could still be observed at a distance of 7-8 mm from the metal surface.

For using a spot technique: the following procedure is adopted; a drop of the mixture of solutions indicated above is placed on filter paper ; if colored paper soaked as described is then placed above an aqueous solution of hydrogen peroxide, then in the respective place, owing to the action of H_2O_2 vapors, there will be observed an increase in density of the blue color.

To get an appreciable effect from hydrogen peroxide (reagent) at a distance of 2 mm takes 10 seconds, while for a 0.3% solution 5 minutes are required.

It has been shown that during atmospheric corrosion of metals (Mg, Al, Zn, Cd, Ni, Mo) hydrogen peroxide is formed. This conclusion has been confirmed by photographic methods [1-3] and by 11 well known reactions for hydrogen peroxide.

The author wishes to thank E.M. Vasileva for her help.

LITERATURE CITED

[1] I.L. Roikh and D.M. Rafalovich, Proc. Acad. Sci. USSR 90, 603 (1953).

[2] I.L. Roikh, Proc. Acad. Sci. USSR 94, 1117 (1954).

[3] I.L. Roikh, Proc. Acad. Sci. USSR 108, 1102 (1956).

Received March 1, 1956

BLANK
PAGE

DISCUSSION

SOME REMARKS APROPOS THE WORK OF I. I. TSAPIV ON OSCILLOGRAPHIC POLAROGRAPHY

Yu. A. Zotov

1) I. I. Tsapiv [1,2,3], has a described a polarographic attachment for an oscillograph in order to obtain polarographic oscillograms for certain ions. To do this I.I. Tsapiv [2, 3], has introduced a factor β – the coefficient of use of the period – and points out that in order to get "optimum results" it should be equal to 0.72 to 0.85. We assume that the author is acquainted with the Berzine - Delahay equation [4], which describes the reversible deposition of metals on a solid electrode during oscillographic polarography. It follows from this equation that the maximum current is directly proportional to the square root of the rate at which the potential is applied.

$$i = kn^{3/2}\, SC_0 \left(\frac{Dv}{T}\right)^{1/2}, \tag{1}$$

where n is the number of electrons participating in the reaction; S is the area of the electrode in cm^2; C_0) solution concentration in M/liter; D is the diffusion coefficient in cm^2/second; T is the temperature in °K; v is the rate at which the potential is applied; and i is the maximum value of the current.

By means of a few transformations it is possible to show that

$$v = \frac{u\omega}{\beta}, \tag{2}$$

where u) is the amplitude of the saw-tooth wave; ω) the frequency of the signal; β-the coefficient of use of the period.

Combining equations (1) and (2) and assuming that the factors n, S, C_0, D, T, ω, u are constant, it can be shown that: $i = k\frac{1}{\sqrt{\beta}}$. Consequently, the current is a linear function of the inverse square root of the coefficient of use of the period. Experiment shows that such a relation only holds for values of β ranging from 0.35 to 0.75 (Fig. 1). We presume that this range should also be the range for optimum values of β.

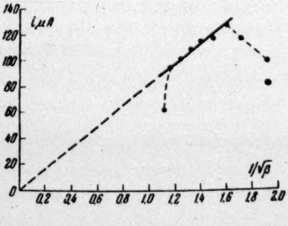


Fig. 1.

It would be interesting to know what I. I. Tsapiv means by "optimum regime" and why he reckons that the best value is between 0.72 and 0.85.

2) Elementary consideration will show that at rates of potential application which are considerably greater than the rate of diffusion of the ions, the region near the electrode will become depleted and consequently there will be a drop in current. Accordingly, oscillographic polarograms should, as a rule, possess a characteristic peak. That an oscillographic polarogram should have such a shape is confirmed by the theory outlined by Delahay [5], and also by the experimental work of Gokhshtein [6], Berzine [4], and others. In this connection a point

worthy of attention is the fact that some of the polarograms obtained by I. I. Tsapiv have no maxima and are similar to ordinary polarograms. This fact is more paradoxical in that it is observed with cations which are reversibly deposited on a solid micro-electrode.

3) When one takes into consideration the attachment proposed by I. I. Tsapiv, the first thing that strikes one is an original and interesting solution of a problem, viz. to use the generator of the oscillograph sweeps for supplying impluses to the electrolytic cell. The scheme is extremely simple and can be prepared without difficulty in any physicochemical laboratory. It is a one-stage amplifier with a load in the cathode circuit or, as it is often called, a cathode repeater. Its presence means that one can tune the output resistance of the generator of the saw-tooth voltage with the resistance of the electrolytic cell.

The author also suggests that the amplifier which he described can be used for applying a saw-tooth voltage, cut below, i.e. with a different coefficient of use of the period to the electrolytic cell. We do not agree with such an idea. It is known that the amplifier of the horizontal sweep of the EO-4 oscillograph is assembled on a paraphase system. Consequently, between each of the horizontally arranged plates and earth a unipolar saw-tooth voltage operates. This voltage is applied to the cathode repeater circuit. Naturally, in order to get interception of the anode current, the tube should be in a closed state. The set-up described however [3], does not gurantee that the tube will operate in this way. In the same article the author gives an operating curve for the tube, which does not correspond to actuality, since on it is shown, not a unipolar, but an alternating saw-tooth voltage. It would be impossible to get such a voltage between the horizontal plates of an EO-4 oscillograph and earth.

We reckon that this attachment, in the form described in [3], would not pair up with the EO-4 oscillograph.

We would be very much indebted if I.I. Tsapiv would give some explanations, and also give some details about the set-up.

LITERATURE CITED

[1] I.I. Tsapiv, Factory Lab. 18, 7 (1952).

[2] I.I. Tsapiv, Factory Lab. 21, 3 (1955).

[3] I.I. Tsapiv, J. Anal. Chem. 11, 63 (1956) (T.p. 59).*

[4] T. Berzine and P. Delahay, J. Am. Chem. Soc. 75, 5 (1953).

[5] P. Delahay, J. Am. Chem. Soc. 75, 3 (1953).

[6] Ya. P. Gokhshtein and Yu. A. Surkov, J. Anal. Chem. 8, 323 (1953) (T.p. 359).*

Received May 16, 1956.

---

* T.p. = C. B. Translation pagination.

BOOK REVIEW

Extraction Methods in the Laboratory. Hecker, Verteilungsverfahren im Laboratorium. Dr. Erich Hecker. XII+229 pp. Verlag Chemie, GMBH Weinheim Bergstr., 1955

Extraction methods are of great importance not only for solving problems in analytical chemistry, but have had wide application in many modern chemical enterprises. The exceptional simplicity of the method, the possibility of using the process as a cycle of operations, the fact that the method can be readily automatized, and the operations remote-controlled have attracted the attention of manufacturers. Thanks to extraction methods, outstanding successes have been achieved in separating elements of similar chemical properties (rare earths : zirconium , hafnium, niobium, tantalum, etc), uranium fission products, amino acids, and many other materials. Extraction methods are widely used radiochemistry for purifying radioactive isotopes and for separating them without carriers. As a method of physicochemical study, extraction has been successfully used for determining the composition and instability constants of complex compounds. The scientific importance of extraction methods, and the number of their practical applications are increasing rapidly.

Accordingly we must welcome the apparance of the monograph under review, the author of which is known for a number of papers on the use of extraction methods. On the basis of his own practical experience, the author has succeeded in making a critical review of the literature published up to the end of 1953, and considers in detail questions relating to the actual techniques and the theory of the different variants of the extraction method.

In the main part (125 pages) which consists of 4 chapters, the fundamental theory of the method and its application in practice is discussed.

The first chapter includes a discussion of the Berthelot - Nernst law, and reasons for deviations of the partition isotherm from linearity are set forth. Since the linear character of the partition coefficient has a favorable effect on efficiency of extraction methods, the author formulates general principles for getting linear partition isotherms of associated and dissociated materials.

On this basis the author affirms that for partition characterized by a linear isotherm, the value of the partition coefficient is a one-valued physicochemical constant, and like the boiling point or melting point, may be used as a characteristic of a substance. Having pointed out the effect of the concentration of the partitioned material, its activity coefficients in both phases, and the temperature on the partition coefficient, the author describes the basic methods of determining this value. Afterwards, taking as an example a model experiment, he sets forth the principles of a multi-stage distribution (multiplikative Verteilung) and introduces the concept of partition index (Verteilungszahl), partition coefficient (Trennfaktor) and volume factor (Volumenfaktor).

The second chapter contains descriptions of the methodological and theoretical foundations of various methods which are based on mixing and subsequent separation of known volumes of immiscible liquids (schubweise Verteilung). The first paragraph of this chapter is devoted to a description of the apparatus used (from simple partition cells, operating on the principle of a U-tube, or on decantation, to completely automatic and very efficient partition batteries, in which, in a short time, hundreds of unit extraction processes may occur. In the second paragraph of this chapter the characteristics of the different variants of the method are discussed:

simple and multiple shaking, as well as considerably more efficient multi-stage methods are given. Of several well known multi-stage laboratory methods, the most widely used one is the Craig method. The theoretical foundations of the Craig process are discussed, taking as an example the separation of a mixture of nicotinamide and benzamide by means of ethyl acetate and water as the immiscible liquids. The author gives quite a lot of space to an exposition of the basis of calculating theoretical partition curves by Craig's method on the basis of known values of the partition indices. In this connection, emphasis should be laid on the great importance of the method described by this author for determining the parition index on the basis of the position of the maximun on the experimental partition curve. Such a detailed discussion of the problem as is given here is justified, since one can reach important conclusions on the fundamental laws of the partition of materials in a given system from a study of the shape of the curves; in addition, on the basis of deviations of the experimental curves from theory one can get information about deviations from conditions laid down by the Berthelot - Nernst law, and about the presence of impurities in the fractions obtained.

Methods of supplemental fractionation (Nachfraktionierung), which are used in addition to the basic process (Grundprozess) are considered just as thoroughly.

Next, descriptions are given of two methods of multiple partition, in which both phases are used in opposite directions, while at the end of each separate partition process some fresh portions of the liquid to be partitioned are introduced. In the O'Keiffe method the latter is introduced into the middle of the apparatus, while in the Vatanab-Morikav method, fresh material is introduced into the inlet of the apparatus. Using the O'Keiffe method as an example, the author illustrates the effect of multiple introduction of material on the shape of the partition curves, and shows graphically how a stationary state develops, and how when this state has been reached, further repetition of the cyclic process does not lead to further changes in the contents of material in the individual fractions.

In the third paragraph of the second chapter, the effect of various factors on the separation of mixtures is considered. Here, the question of the effect of the partition coefficient on the number of elementary stages necessary for complete separation of mixtures is treated in detail; the concept of the partition function (Trennfunkti is formulated; the efficiency and field of application of methods of supplementary fractionation are characterized; and cases are described of the application of a completely automatic apparatus for Craig distribution, in particular for separation of multi-component systems; finally approximate methods fo calculating theoretical partition curves are described. Questions relating to the efficiency and field of application of partition according to the O'Keiffe and Vatanab - Morikov variants are considered briefly.

In discussing the significance of the chemical structure of materials for extraction methods, the author correctly points out the great complexity of the interconnections between the behavior of the partitioned material and the properties of both phases. At the moment, it is impossible to formulate any general principles relating to inorganic materials. As for organic materials, here a few regularities have been established which allow one, in some instances, to depart from a purely arbitrary approach for selecting a solvent for a particular extraction. In particular, a study has been made of the effect of the nature of substituents and the length of the carbon chain of an organic compound, on the value of its partition coefficient between water and an organic solvent. The author emphasized the influence of molecular volume interaction between dissolved material and solvents (in particular, formation of hydrogen bonds) on the value of the partition coefficient. The author believes that a decisive factor for extraction of inorganic ions is their solvation. It is precisely from this point of view that he considers the effect of additions of organic complexing agents, e.g. 8-hydroxyquinoline, on the extractability of inorganic ions. Further, the question of the connection between partition coefficient and characteristics of the solvent is discussed in detail. Here is noted the great importance of differences in the chemical structures of the partitioned materials, and the miscibility of the solvents, on the partition coefficient. The miscibility of the phases is of great importance for separation of organic materials: partition coefficients, as a rule, increase with decreasing miscibility. By linking this rule with intermolecular interactions between solvents, the author assigns them to 5 classes; which class they belong to is determined by the number and stability of hydrogen bonds formed. The thixotropic series classified in this way is of great practical importance, since it facilitates a conscious selection of solvents on the basis of their miscibility. The concluding paragraph is devoted to questions of the use and mechanism of buffer solutions and complexing agents which are of importance for determining conditions for separating materials by extraction methods.

The fourth paragraph of the second chapter is devoted to the analytical uses of Craig partition (test for purity, identification and determination of the molecular weight of materials).

The third chapter contains various pieces of information on partition by even movement of phases (Gleichförmige Verteilung), which has achieved wide application as a method for industrial separation of mixtures.

In the fourth chapter which ends the general part, the limitations of the use of multiple partition are indicated, and general principles are formulated for combining the various methods of fractionating materials. As is known, by combining the various methods, it is possible to attain several million fold enrichment during separation of natural materials (carotinoids, oxytocins, etc) from biological materials.

In a special part (50 pages) consideration is given to the very important question of the practical choice of solvents for extraction separation of mixtures,, which are capable of giving optimum conditions for extraction; numerous actual examples are given of separation of organic and inorganic materials.

The appendix (14 pages + XII pages) includes examples of Craig partition curves and tables of mathematical functions which are useful for calculations in extraction methods; information is given on limited miscible vapors of organic solvents and classification of separation methods.

The book ends with a bibliography and an index. The bibliography covers the literature up to the end of 1953. In the vast bibliography (525 references) only one reference is made to the work of Soviet authors (the article by V.I. Kuznetsov, 1947). The later work of V.I. Kuznetsov and that of other Soviet authors (I.P. Alimarin, A.G. Karabash, A.K. Babko, F.G. Zharovsky, B.V. Nekrasov, etc.) are left out.

The monograph barely touches on the results of modern work on the use of extraction methods for studying the composition and stability of complex compounds, for analytical separation of elements, for preparing radioactive elements without carriers.

A rather unfortunate arrangement of materials complicates reading of the book.

Despite these drawbacks, the book under review is of undoubted interest as a valuable compendium of accumulated experience gained both in the theory and practice of extraction methods.

In the opinion of the reviewers, a translation of this book into Russian is very desirable, but it should be supplemented by references to the work of Soviet scientists which had been carried out prior to 1953, and also by references to the numerous new theoretical and experimental studies of a number of authors (V.I. Kuznetsov, I.M. Korenman, F.V. Zaikovsky, Rossoti, Irving, etc.). Hekker's book, supplemented with such material, will find wide response from scientific workers, chemical engineers, and specialists in related sciences.

A.I. Busev and N. G. Polyansky

BLANK
PAGE

OBITUARY

EVGENY STEPANOVICH PRZHEVALSKY

On the twenty-first of July, 1956, in his seventy-eighth year, one of the oldest analytical chemists of our country, Professor Evgeny Stepanovich Przhevalsky, Doctor of Chemical Sciences, died.

He was born in January 1879 near the town of Pereyaslav Khmelnitsky.

On finishing his course at the Nezhinsky classical high school in 1897, he proceeded in 1898 to the natural sciences section of the physicomathematical faculty of Moscow State University, where he graduated in 1903 with first-class honors.

Dating from this time, his acivity was closely bound with Moscow State University to which he devoted more than 50 years of his life.

He specialized in organic chemistry under the direction of Prof. V.V. Markovnikov, and in 1903 published his first paper in the Journal of the Russian Chemical Society on "Alpha Methyladipic Acid." He transferred in 1904 to the laboratory of Prof. N. D. Zelinsky with whom he worked for several years, carrying out in the course of this time a series of studies in organic chemistry.

In 1910 he became an assistant in the department of organic and analytical chemistry of Moscow State University, where he supervised the students in qualitative and quantitative analysis.

Simultaneously with his teaching work at the university he was also a lecturer in chemistry for higher courses for women in 1913; from 1918 to 1922 he was a lecturer in the Institute of Communication Engineers. For 10 years (from 1904 to 1914) he gave free instructions in evening classes for workers. In 1928 he was confirmed as a lecturer at Moscow University, where he took the course on "Methods of Chemical Analysis.. In 1929, he took an active part in organizing a chair of analytical chemistry which he headed from 1930 to 1953.

He is the creator of a school of analysts at Moscow State University, where, under his direction, analytical chemistry was developed as a special study in the chemistry faculty.

He never restricted his work to the university. In 1918 he took an active part in organizing the Institute of Pure Chemical Reagents, and over a period of years participated actively in its work; he was successively a member of the board, assistant director on the scientific side, and head of the analytical section; he served as a consultant up to the last years of his life. In the Institute of Pure Reagents, Przhevalsky was the organizer of work on standardizing the quality of chemical reagents, as a result of which more than 200 standards were issued for reagents of various grades. It was here that he started work on determination of small amounts of materials by means of organic reagents he continued with this work in the analytical chemistry department of Moscow State University, and developed it successfully. During his last years, his interests were centered on the analytical chemistry of rare elements. The last studies carried out under his direction related to the use of β-diketones in the analytical chemistry of beryllium, and investigation on the quantitative determination of titanium in titanium ores and concentrates.

In addition to his scientific work and teaching activities, he edited a number of textbooks and manuals on analytical chemistry, including Ber-Lunge's Chemicotechnical Methods"; Kolthoff and Laitinen's "Determination of Hydrogen Ion Concentration and Electrotitration." He was a member of the editorial board of "Factory Laboratories" and the "Journal of Analytical Chemistry" for many years, and also reviewed many books on qualitative and quantitative analysis.

He was a member of the editorial board of "Factory Laboratories" and of the Journal of Analytical Chemistry" for many years, and also reviewed many books on qualitative and quantitative analysis.

He has received the following government awards: Order of Lenin; Medal of Honor; and medals for "Glorious Work in the Great Patriotic War 1941-1945" and "The 800th Anniversary of Moscow."

He has brought up a large number of analytical chemists who have gained success in scientific-research institutes and industrial enterprises.

All his students and everybody who came in contact with him will long remember him as a great scientist, an attentive and considerate man.

A. I. Busev and N. G. Polyansky

ACADEMY OF SCIENCES, USSR

CHEMICAL SCIENCES SECTION

PRIZES TO BE AWARDED FOR COMPETITIONS BY THE ACADEMY OF SCIENCES, USSR

The Chemical Sciences Section of the Academy of Sciences, USSR announces its intention of awarding the following prizes.

1) a D. I. Mendeleev Prize of 20,000 rubles for original theoretical studies and scientific work of great practical importance;

2) an N. D. Zelinsky Prize of 10,000 rubles for outstanding scientific work in the field of organic chemistry and the chemistry of petroleum.

These prizes will be awarded by the Praesidium of the Academy of Sciences, USSR as a result of competitions which can be entered by Soviet citizens, collectives, and Soviet scientific institutions.

Work can be entered by scientific societies, scientific-research Institutes, higher educational establishments, social organizations, and individuals.

Only published work can be accepted.

Two copies of the papers should be sent to the Chemical Sciences Section of the Academy of Sciences, USSR (Moscow, B-71, B. Kaluzhskaya, 14) and should be entitled "Competition for the D. I. Mendeleev (N. D. Zelinsky) Prize;" an author's abstract (approximately $^1/_4$ the length of the paper) should be included, as well as concise bibliographical information about the candidate for the prize, listing his most important scientific work and inventions.

Last date for entries to be received April 1, 1957.

Academy of Sciences, USSR
Chemical Sciences Section

BLANK
PAGE

TABLE OF CONTENTS (continued)

	Page	Russ. Page
18. Determination of Monoethanolamine, Diethanolamine, and Triethanolamine in Their Mixtures By Partition Chromatography. D. A. Vyakhirev and Yu. N. Suloev	793	739
19. A Photocolorimetric Micro Method of Determining Lactose and Saccharose When They are Present Together. IV. M. N. Tulchinsky	797	742

Brief Communications

	Page	Russ. Page
20. Methods for the Isotopic Analysis of Water. 1. A New Apparatus for the Falling Drop Method of Isotopic Analysis of Water. A. I. Shatenshtein and Ya. M. Varshavsky	803	746
21. Iodometric Determination of Iodides. B. I. Leonov	807	749
22. A Bismuthate Method for Determining Chromium in Steels not Containing Vanadium. P. F. Agafonov	811	752
23. A New Color Reaction for Divalent Cobalt. G. D. Nessonova and E. K. Pogosyants	813	754
24. A Highly Sensitive Reaction for Hydrogen Peroxide. I. L. Roikh	815	755

Discussion

	Page	Russ. Page
25. Some Remarks Apropos the Work of I. I. Tsapiv on Oscillographic Polarography. Yu. A. Zotov	817	756

Book Review

	Page	Russ. Page
26. Extraction Methods in the Laboratory. Hecker	819	758

Obituary

	Page	Russ. Page
27. Evgeny Stepanovich Przhevalsky	823	761

USSR Academy of Sciences, Chemical Sciences Section

	Page	Russ. Page
28. Prizes to be Awarded for Competitions by the USSR Academy of Sciences	825	776